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Geology and geochemical characteristics of Gevaş listwaenites (Van-Turkey)

Gevaş listvenitlerinin jeokimyasal özellikleri ve jeolojisi (Van-Türkiye)

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ABSTRACT

This study investigates the geological, mineralogical, and geochemical characteristics, and the precious metal contents of the listwaenite in the Gevaş ophiolite. Gevaş listwaenites are found to be mainly composed of dolomite/ankerite, quartz and chalcedony. Calcite, magnesite, chlorite, fuchsite, magnetite, pyrite, hematite and chromite were found as the primary minerals, and tetrahedrite, chalcopyrite, galena, pyrite, millerite, sphalerite, argentite, gold and magnetite were determined as opaque minerals in ore bearing listwaenite (OBL). Covellite, chalcosite, malachite, azurite, anglesite, cerussite, violoarite, bindheimite and limonite were found as secondary minerals. The listwaenites formed by alteration of the serpentinites (n=23 sample) were depleted in MgO, Fe_2O_3, Na_2O and enriched in K_2O, CaO and H_2O with respect to serpentinite. The values of SiO_2 and Al_2O_3 were variable in serpentinite and listwaenite, with respect to their average content, and the MnO values were enriched only in OBL. Listwaenites were classified into two groups based on their SiO_2 content: (i) Silica-rich listwaenites being named as Type I, SiO_2>35.52wt.%, and (ii) SiO_2≤35.52 wt. % carbonate-rich listwaenites being named as Type II. The Cr, Ni and Co contents of listwaenites (OBL) were depleted according to serpentinite, but the listwaenites wenriched in Au, Ag, Cu, Zn, Sb, As, K, Rb, Ba, Sr, P, Ti, U and Pb contents. The geological, mineralogical and geochemical studies revealed that those listwaenites that have limited cracks and fissures do not show metal enrichment, whereas well sheared and thrust related listwaenite zones are enriched in Au, Ag, Cu, Sb, Zn and Pb metals. While gold and silver show positive correlations with As, Ba, Cu and Sb (i.e. r >0.93), Pb, Zn and Ni show lower correlations. A limited number of analyses indicate that the Au value of Gevaş listwaenites is 53 times more gold-enriched than the serpentinized peridotites.

Keywords: Geochemistry, gold, listwaenite, ophiolite, Van.

ÖZ

Bu çalışmada, Gevaş ofiyoliti ile ilişkili gözlenen listvenitlerin jeolojik, mineralojik, jeokimyasal karakteristikleri ile değerli metal içerikleri incelenmiştir. Gevaş listvenitlerinin ana mineralojik bileşimini; dolomit/ankerit, kuvars, kalsedon ve az miktarda kalsit, manyezit, klorit, fuksit ve opak minerallerden manyetit, pirit, hematit ve kromit oluşturmaktadır. Cevherli listvenit zonunda tetraedrit, kalkopirit, galenit, pirit, millerit, sfalerit, arjantit, altın ve manyetit birincil opak minerallerdir. Kovelin, kalkosin, malakit, azurit, anglezit, seruzit, violoarit, bindheimit ve limonit ikincil olarak oluşmuşlardır. Serpantinitlerin alterasyonu ile oluşan listvenitler (n=23 örnek), ortalama serpantinitlere göre MgO, Fe_2O_3, Na_2O gibi ana oksitlerce fakirleşmişken, K_2O, CaO ve H_2O bakımından zenginleşmiştir. Listvenitle-

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rin ortalama SiO_2 ve Al_2O_3 değerleri, serpantinitlerin ortalama değerlerine göre değişkenlik gösterir. MnO sadece cevherli listvenitlerde zenginleşmiştir. Listvenitler SiO_2 içeriklerine göre iki alt gruba ayrılmıştır; (i):silis içeriği %35.52'den büyük olan silisleşmiş listvenitler, Tip I, (ii): silis içeriği %35.52'den küçük veya eşit olan silika-karbonat listvenitler (Tip II) olarak tanımlanmıştır. Tüm listvenitlerin Cr, Ni ve Co içerikleri serpantinitlere göre daha düşükken hidrotermal çözeltilerden etkilenmiş listvenitler Au, Ag, Cu, Zn, Sb, As, K, Rb, Ba, Sr, P, Ti, U ve Pb elementleri bakımından zenginleşmiştir. Jeolojik, mineralojik ve jeokimyasal çalışmalara göre, sınırlı kırık ve çatlak içeren listvenitlerde metal zenginleşmesi gözlenmezken, makaslamaya uğramış ve bindirme cephelerine yakın listvenitlerde Au, Ag, Cu, Sb, Zn ve Pb metalleri bakımından zenginleşme saptanmıştır. Altın ve gümüş değerleri ile As, Ba, Cu ve Sb arasında pozitif bir ilişki gözlenirken, Pb, Zn ve Ni ile düşük korelasyon katsayısına sahip ilişkiler görülür. Alınan sınırlı sayıdaki örnekler Gevaş listvenitlerinin Au değerinin serpantinleşmiş ultramafitlere göre 53 kat zenginleştiğini ortaya koymaktadır.

Anahtar Kelimeler: Jeokimya, altın, listvenit, ofiyolit, Van.

INTRODUCTION

The term Listwaenite was first introduced to the literature by Rose (1837) from a study of the Ural area; it is defined as a silica-carbonate enrichment of peridotites. The most fundamental preliminary studies on this listwaenite were conducted by Russian geologists and the others (Ploshko, 1963; Kashkai and Allakhverdiev, 1965, 1971; Scherban, 1967; Scherban and Borovikova, 1969; Goncharenko, 1970, 1984; Sazanov, 1975; Abovian, 1978; Kuleshevich, 1984; Spiridinov, 1991). Similarly, listwaenites have been described as carbonitized and silicified serpentinites (Buisson and Leblanc, 1985). Listwaenites are formed by intermediate-to-low temperature hydrothermal/metasomatic alteration of mafic-ultramafic rocks, and are commonly located within or near major faults and shear zones (Halls and Zhao, 1995). Listwaenites typically contain quartz, carbonate minerals (magnesite, ankerite and dolomite) and/or fuchsite, together with sulphides and other hematite, magnetite, cobalt minerals and chromite relicts. With some exceptions, they are formed by the metasomatic/hydrothermal alteration of serpentinite (Kashkai and Allakhverdiev, 1965; Capedri and Rossi, 1973; Buisson and Leblanc, 1986; Tsikouras et al., 2006). SiO_2, CaO, MgO and Fe_2O_3 are the most common oxides determined in listwaenite. Listwaenite exploration has theoretical and practical importance worldwide, because listwaenites bear gold, arsenic, cobalt, nickel, wolfram and mercury mineralization (Zhelobov, 1979; Kashkai and Allakhverdiev, 1965; Buisson and Leblanc, 1986; Korobeynikov and Goncharenko, 1986; Leblanc and Lbouabi, 1988; Leblanc and Fischer, 1990; Auclair et al., 1993; Sherlock and Logan, 1995; Halls and Zhao, 1995). However, in terms of metal enrichment for economical purposes, the gold content of listwaenites, both in the world and in our country, is very low. Kaymaz Village, in the Eskişehir-Sivrihisar province has the only known economically and profitable listwaenite type deposits in Turkey, with a reserve of 974.000 tonnes of grade 6.04 g/t Au (Gözlem Dergisi, 2000). The Koza Mining Company is working on this site as a new owner of the gold deposit in Kaymaz village.

Other known listwaenite zones in Turkey, such as Bursa-Sülüklügöl, Eskişehir-Mihalıççık and Karacakaya, Uşak-Muratdağ, Kars-Kağızman, Sivas-Divriği, Erzincan-Kızıldağ, Malatya-Karakuz and Güvenç, Isparta-Şarkikaraağaç and Bitlis-Mutki, are not economically important. They have low grades of precious metal and base metal contents (e.g., Aydal, 1989; Erler and Larson, 1990; Tüysüz and Erler, 1993; Boztuğ et al., 1994; Koç and Kadıoğlu, 1996; Gözler et al., 1997; Uçurum 1998; 2000; Uçurum and Larson, 1999; Çiftçi, 2001; Başta et al., 2004; Akbulut et al., 2006). Listwaenites in the Erzurum-Narman area are enriched mostly in Hg and As contents (Genç et al., 1990). The association of Co, Ni, As, Hg, Au and Ag with listwaenites at ultramafic-mafic belts in Turkey is well presented by Uçurum (2000). Metal paragenesis similar to this study conforms to listwaenites in Kyrgyzstan, Armenia and the Sivas-Alacahan area in Turkey (e.g., Kashkai and Allakhverdiev, 1965; Boztuğ et al., 1994).

This study presents the geological, mineralogical and geochemical characteristics of the Gevaş listwaenites and discusses its precious metal content with an exceptional mode of paragenesis regarding its lead enrichment. These listwaenites are observed as tectonically controlled with ultramafic rock sequences, along an E-W direction to the south of Lake Van (Figure 1).

GEOLOGY

The Eastern Anatolia Region is one of the best examples in the world of a continental collision zone. This continent-continent collision is marked by the Bitlis-Zagros fold and thrust belt (see Figure 1); the collision of the Arabian and Eurasian plates began in the Middle-Miocene (Şengör and Yılmaz, 1981). The Eastern Anatolian Accretionary Complex (EAAC) forms a 150-180 km wide, NW-SE extending belt in the middle of the region. (Şengör et al., 2003). The dominant and active structures of the East Anatolian High Plateau are NE-SW and SE-NW trending strike-slip faults and E-W striking thrust faults (Şengör et al., 1985). The Eastern Anatolian High Plateau also comprises one of the high plateaus of the Alpine-Himalaya mountain belt, with an average elevation of approximately 2 km (Keskin, 2003; Şengör, 2002).

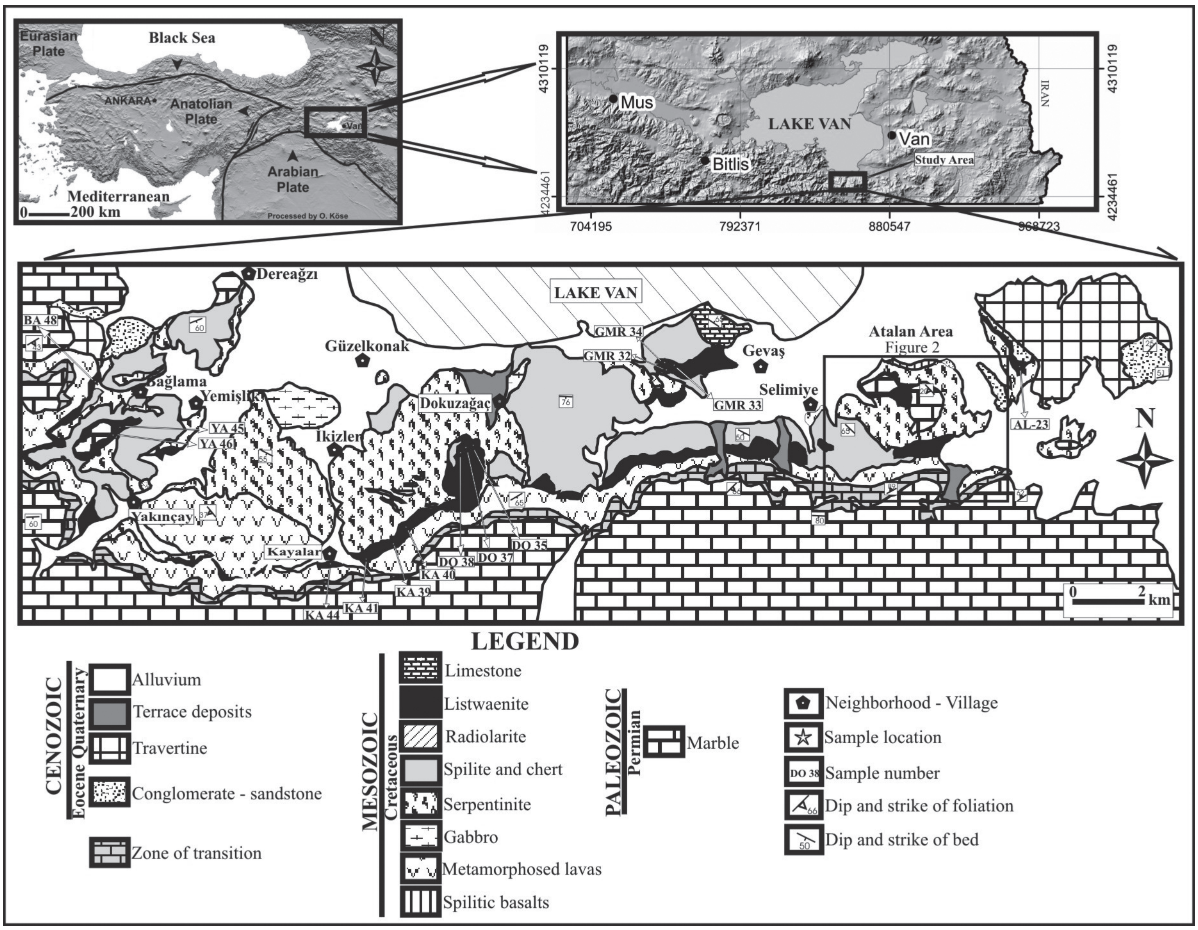


Figure 1. Geological map of the study area (modified from Yılmaz et al., 1981).
Şekil 1. Çalışma alanının jeoloji haritası (Yılmaz vd., 1981'den değiştirilerek).

The study area covers the south side of the Lake Van basin. This area is mostly formed by metamorphic rocks of the Bitlis Massive and by Gevaş ophiolitic rocks. The Bitlis Massive is located to the south of the basin and has been investigated by many researchers (Yılmaz, 1975, 1978; Boray, 1975, 1976, Yılmaz et al., 1981; Göncüoğlu and Turhan, 1983, 1985; Şengör and Yılmaz, 1981; Tolluoğlu and Erkan, 1982; Şengün, 1984; Şengün et al., 1991). The Bitlis Massive is composed of various compositions of schist and gneiss . The ophiolites are exposed just south of Lake Van and extend along an E-W direction near Gevaş town. In this region, four tectonic units have been determined (Yılmaz et al., 1981). These are an ophiolite association, the metamorphic rocks of the Bitlis Massive, a transition zone between the ophiolites and metamorphic rocks, and an overlying sedimentary cover (Yılmaz et al., 1981). The ophiolites are obducted on a continental crust at the Late Cretaceous, with imbricate slices, and are present among the metamorphic rocks of the Bitlis Massive (Yılmaz, 1978).

During this obduction, some metamorphism along a 500-1000 m thick transition zone occured. Ophiolites are widely observed around Atalan, Dokuzağaç and İkizler villages. So, after the emplacement of an alteration product in the region (as a result of hydrothermal alteration), there are yellow-brown coloured rocks extending in an E-W direction, and these have been described as listwaenites. The listwaenite is not only associated with serpentinities, but also observed at the contact of spilite, chert and metamorphosed lavas in the south. This means that after the listwaenite formation in the area, listwaenites were tectonically controlled by the other units (Figure 2). In the transition zone, calc-schist, epidote glocophane schist and quartz serisite schist have been described near the Atalan area. Eocene aged conglomerate and sandstone are present in the NE of the Atalan Vilage (see Figure 2).

Metal enrichment was determined only in the listwaenite zone near Atalan Village (see Figure 2). This ore-bearing listwaenite (OBL) has been tectonically effected by thrust and shearing events. Fault planes are observed in N45^{0}W/45^{0}SW and N45^{0}E/50^{0}SE directions (Figure 3a). The main thrust direction in the region is E-W, but this direction varies locally.

ANALYTIC METHODS

31 listwaenite and 15 wall-rocks, such as serpentinite, spilite, marble and schist samples were obtained to determine their mineralogical, petrographical and geochemical characteristics. These samples were ground and analyzed at the ALS Chemex Analytical Laboratories in Canada (Tables 1 and 2). Analyses were carried out in two stages (i.e. in 2005 and 2006). The analyses of the first stage were carried out from the wide area (see Figure 1). The second stage analyses were made from the samples from the Atalan area and its surroundings (sample no AT 1 - AT18 composed of 12 listwaenite, 2 spilite, 1 marble and 3 schist samples, see Figure 2). An X-Ray-Fluorescence (XRF) method was used for all major oxides, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used for trace element analyses. The detection limits for major oxides and for trace elements are shown in Tables 1 and 2. For gold analysis, Au was analysed by fire assay and Atomic Absorbtion Spectrometer (AAS). Although 46 samples were collected, the results of analyses obtained from only 36 samples (i.e. 27 listwaenite samples and 9 wall-rocks of 3 serpentinite; 2 spilite; 1 marble and 3 schist) are presented in this study. Details of the analytical procedure are given in Moss and Scott (1996).

PETROGRAPHICAL STUDIES

Ophiolite Units

Ophiolites are exposed at Atalan, Şalıgöl and Aladüz villages and at Baklakör Hill (see Figure 2). The serpentinites here have a massive appearance, are greenish black color and have a wax-like lustre (Figure 3b). They are mainly harzburgitic in composition and contain some relict chromites. Olivine and bastitized pyroxenes can be determined macroscopically. Spilitic basalts crop out in the Atalan area. The open space of spilites is filled by quartz carbonate minerals (Figure 3c). These spilites

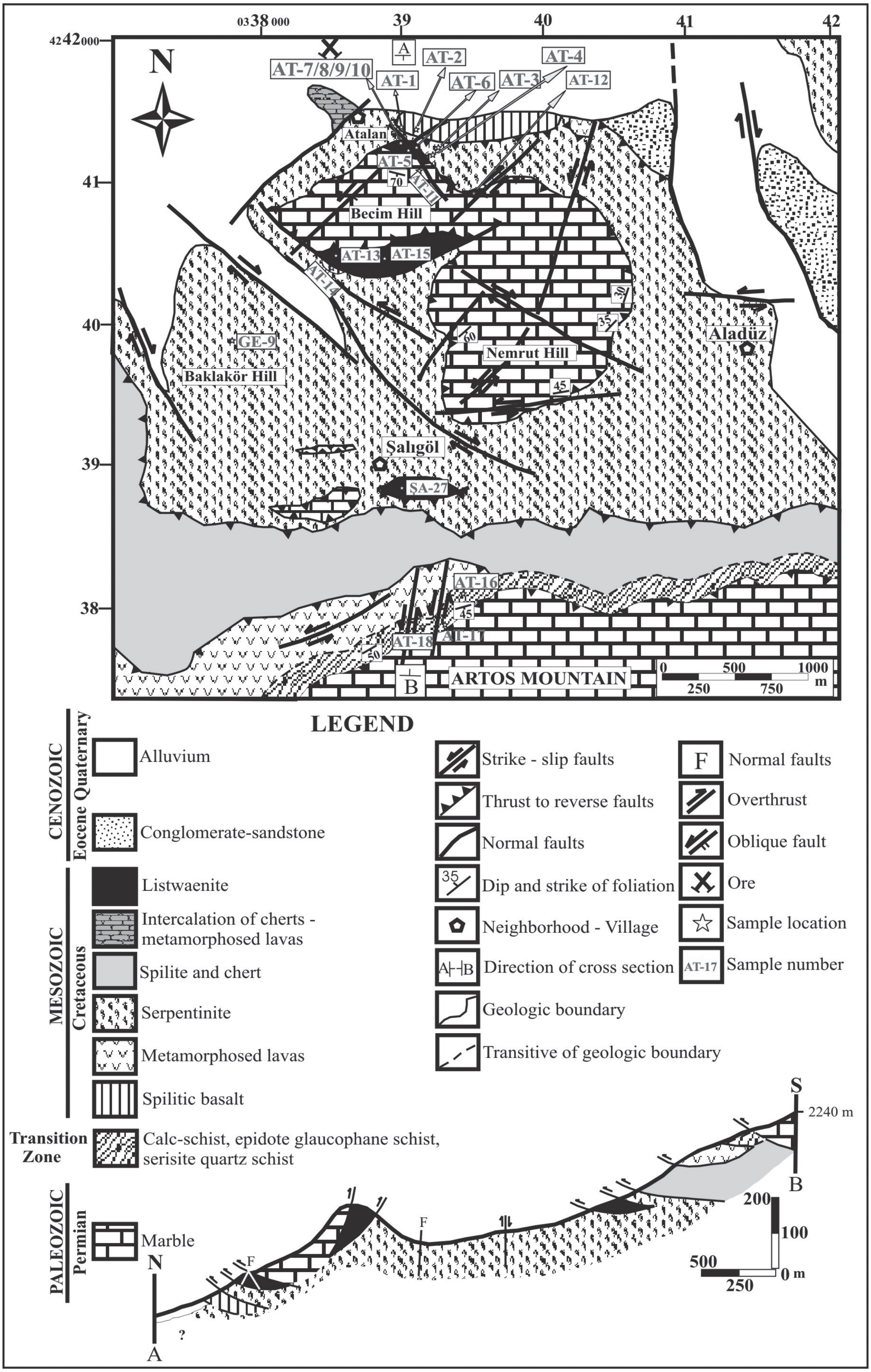


Figure 2. Geological map and cross-sections of the Atalan area.

Şekil 2. Atalan sahasının jeoloji haritası ve kesiti.

Table 1. Major oxide concentrations of the rocks in the study area.
Çizelge 1. Çalışma alanındaki kayaçlardan elde edilen ana oksit değerleri.

Rock Type	LI	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII
Sample no.	AT-5	AT-6	AT-12	AT-13	AT-15	AT-24	AT-25	AT-26	AL-23	ŞA-27	GR-32	GR-33	GR-34	DO-35	DO-37	DO-38
SiO_2	43.43	26.74	31.56	33.38	9.34	28.14	29.91	34.31	32.72	29.48	27.77	31.54	17.33	27.01	24.08	42.01
Al_2O_3	0.78	3.48	1.04	0.70	0.24	0.97	1.29	0.38	1.37	0.68	4.03	0.82	0.59	0.37	0.32	1.23
Fe_2O_3	5.58	4.41	5.70	6.58	3.17	7.76	6.62	7.12	5.21	6.27	4.27	5.54	5.24	6.66	7.07	8.13
CaO	12.18	29.84	31.09	3.44	30.14	6.12	1.64	10.69	21.17	4.31	31.77	21.05	23.39	1.50	0.73	15.50
MgO	12.01	2.53	1.18	24.57	14.52	22.93	27.94	14.13	10.32	26.09	1.73	10.87	15.75	28.40	31.26	9.62
Na_2O	0.15	0.11	0.08	0.19	0.03	0.09	0.12	0.10	0.08	0.18	0.09	0.05	0.10	0.18	0.16	0.06
K_2O	0.21	0.98	0.15	0.11	0.03	0.39	0.32	0.13	0.29	0.17	1.12	0.15	0.11	0.11	0.08	0.07
Cr_2O_3	0.18	0.13	0.27	0.21	-0.01	0.21	0.24	0.23	0.25	0.25	0.13	0.21	0.12	0.26	0.29	0.41
TiO_2	0.03	0.23	0.02	0.02	0.01	0.01	0.02	-0.01	0.06	0.01	0.23	0.03	0.02	0.01	-0.01	0.01
MnO	1.01	1.13	0.09	0.09	0.10	2.07	0.12	2.07	0.13	0.13	0.24	0.12	0.14	0.11	0.12	0.12
P_2O_5	0.01	0.08	0.01	-0.01	0.11	0.02	-0.01	-0.01	0.02	-0.01	0.07	-0.01	0.01	0.05	0.06	0.01
SrO	0.03	0.02	-0.01	0.02	0.03	0.04	0.01	0.05	0.03	0.02	0.01	0.03	0.03	0.01	-0.01	0.01
BaO	-0.01	0.03	0.01	-0.01	0.01	-0.01	-0.01	0.03	0.01	-0.01	0.01	-0.01	-0.01	-0.01	-0.01	-0.01
LOI	23.80	28.60	26.90	30.40	41.80	31.20	31.10	24.20	28.30	32.30	27.80	29.50	37.10	35.20	35.80	22.80
Total	99.39	98.31	98.09	99.69	99.52	99.94	99.31	93.42	99.96	99.87	99.27	99.89	99.92	99.86	99.94	99.97

Rock Type	LII	LII	LII	LI	LII	LI	LII	SPL	SPL	SER	SER	SER	MRB	EGSC	CSC	SQSC
Sample no	KA-39	KA-40	KA-41	KA-44	YA-45	YA-46	BA-48	AT-1	AT-2	AT-3	AT-4	GE-9	AT-11	AT-16	AT-17	AT-18
SiO_2	26.65	16.92	21.38	48.71	34.36	37.35	24.82	34.49	44.76	32.92	36.98	36.66	0.61	41.38	65.34	81.00
Al_2O_3	0.74	0.67	0.51	0.98	0.30	1.40	0.49	11.23	14.08	1.20	1.36	1.05	0.17	14.60	0.86	7.47
Fe_2O_3	5.35	3.90	4.79	5.17	4.44	4.02	6.86	8.70	12.41	9.43	8.55	8.59	0.45	14.06	0.76	3.92
CaO	15.88	23.36	25.76	5.63	18.40	17.88	3.57	18.33	8.30	0.38	0.59	0.56	53.51	7.43	17.21	0.35
MgO	17.89	16.72	12.82	16.07	13.02	11.74	28.42	4.85	4.47	39.11	38.05	37.56	0.47	6.03	0.17	2.16
Na_2O	0.14	0.17	0.03	0.56	0.07	0.28	0.13	3.40	3.58	0.21	0.19	0.25	-0.01	3.30	0.11	2.45
K_2O	0.09	0.06	0.06	0.04	0.03	0.23	0.11	0.64	1.13	0.03	0.03	0.09	0.01	1.70	0.16	0.44
Cr_2O_3	0.27	0.34	0.31	0.19	0.54	0.40	0.28	0.03	0.08	0.32	0.34	0.35	-0.01	0.03	-0.01	-0.01
TiO_2	0.01	0.02	-0.01	0.10	0.01	0.08	-0.01	1.57	1.77	0.02	0.02	0.05	0.02	4.48	0.06	0.35
MnO	0.13	0.08	0.12	0.12	0.10	0.12	0.12	0.12	0.18	0.12	0.13	0.10	0.01	0.20	0.04	0.11
P_2O_5	-0.01	0.01	0.01	0.08	0.04	0.01	0.01	0.24	0.41	0.02	0.01	-0.01	0.06	0.81	0.06	0.20
SrO	0.06	0.04	0.03	0.02	0.11	0.06	0.01	0.03	0.03	-0.01	-0.01	-0.01	0.01	0.02	0.02	-0.01
BaO	-0.01	-0.01	0.01	-0.01	-0.01	0.01	-0.01	0.02	0.01	-0.01	-0.01	-0.01	-0.01	0.03	-0.01	0.01
LOI	32.70	37.70	34.20	22.30	28.50	26.40	35.10	14.90	8.69	14.35	13.65	14.45	43.40	5.93	14.50	1.48
Total	99.89	99.98	100.02	99.96	99.91	99.98	99.90	98.55	99.90	98.09	99.88	99.68	98.69	100.00	99.27	99.92

Dedection limit is 0.01 wt % for all major oxides, LI:Type I listwaenite, LII: Type II listwaenite; SPL: spilite, SER: serpentinite, MRB: marble, EGSC: epidote glaucophane schist, CSC: calc-schist, SQSC: serisite quartz schist

Table 2. Trace element concentrations of the listwaenites and other rock types in the study area.
Çizelge 1. Çalışma alanındaki kayaçlardan elde edilen ana oksit değerleri.

Rock Type	LI	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII	LII
Sample no./ Dedection limit	AT-5	AT-6	AT-7	AT-8	AT-9	AT-9	AT-12	AT-13	AT-13	AT-24	AT-25	AT-26	AL-23	ŞA-27	GR-32	GR-33	GR-34	DO-35
Rb (0.1ppm)	21.40	82.00	62.90	56.20	6.50	6.50	7.60	3.40	3.40	6.20	4.90	3.00	2.90	2.20	6.70	1.40	0.90	0.90
Th (0.2ppm)	-0.20	1.60	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	-0.20	0.20	-0.20	0.30	-0.20	-0.20	-0.20
U (0.05ppm)	0.20	1.10	0.30	0.10	0.10	0.10	0.20	0.10	0.10	0.08	-0.05	0.47	0.23	-0.05	0.30	0.23	-0.05	-0.05
Ta (0.05ppm)	-0.05	0.18	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
La (0.2ppm)	-0.50	9.40	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	0.20	-0.20	0.20	0.70	-0.20	0.90	0.90	0.20	-0.20
Ce (0.05ppm)	0.58	17.85	0.32	0.26	0.46	0.46	0.51	0.29	0.29	0.49	0.07	0.50	1.34	0.14	1.26	1.65	0.47	0.25
Sr (0.2ppm)	320.00	252.00	105.50	178.50	273.00	273.00	43.80	103.50	103.50	250.00	76.70	516.00	276.00	171.50	76.40	293.00	266.00	48.90
Zr (0.5ppm)	0.70	20.00	0.80	-0.50	-0.50	-0.50	-0.50	0.60	0.60	-0.50	-0.50	-0.50	-0.50	-0.50	1.00	-0.50	-0.50	-0.50
Y (0.05ppm)	1.50	6.60	1.30	1.20	1.00	1.00	1.00	0.60	0.60	1.34	0.84	0.98	1.24	0.48	7.45	2.29	2.16	0.34
Hf (0.02ppm)	-0.10	0.60	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10	-0.02	-0.02	-0.02	-0.02	-0.02	0.03	-0.02	-0.02	-0.02
Nb (0.05ppm)	0.20	2.90	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.05	-0.05	-0.05	0.05	-0.05	-0.05	0.09	0.06	0.09
P (10ppm)	50.00	330.00	10.00	20.00	10.00	10.00	80.00	20.00	20.00	20.00	10.00	20.00	60.00	20.00	270.00	30.00	-10.00	180.00
Ti *	0.01	0.06	0.01	0.01	-0.01	-0.01	0.01	0.01	0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
Ba (10ppm)	50.00	200.00	870.00	70.00	150.00	150.00	10.00	10.00	10.00	60.00	10.00	350.00	20.00	10.00	40.00	50.00	10.00	70.00
K *	0.21	0.92	0.49	0.42	0.05	0.05	0.21	0.08	0.08	0.06	0.05	0.03	0.06	0.04	0.13	0.02	0.02	0.02
Mn (5ppm)	6270.00	6140.00	11500.00	4030.00	11000.00	11000.00	553.00	629.00	629.00	10650.00	736.00	12550.00	681.00	716.00	1185.00	654.00	624.00	574.00
Mo (0.05ppm)	0.95	1.45	0.38	0.39	0.34	0.34	0.56	0.34	0.34	0.50	0.33	0.58	0.61	0.42	1.56	0.39	0.27	0.33
Ca *	8.72	21.50	2.22	2.62	4.97	4.97	22.30	2.58	2.58	4.15	1.03	7.19	15.20	3.00	21.30	14.95	16.00	0.72
Mg *	6.92	1.48	10.55	12.70	11.50	11.50	0.65	14.85	14.85	11.50	13.65	7.23	5.56	13.10	0.83	5.87	8.26	15.10
S*	0.23	0.02	0.32	0.13	0.26	0.26	0.01	-0.01	-0.01	0.19	-0.01	0.64	0.03	0.03	-0.01	0.01	-0.01	0.01
Ag (0.01ppm)	8.01	1.40	176.00	1.16	12.00	12.00	0.06	0.06	0.06	8.32	0.12	43.60	0.02	0.06	0.50	0.03	0.01	0.06
As (0.1ppm)	97.40	65.00	483.00	24.60	52.90	52.90	119.00	5.80	5.80	41.00	5.60	182.00	481.00	86.30	829.00	17.00	9.00	7.30
Au** (5ppb)	81.00	75.00	267.00	30.00	30.00	30.00	-5.00	-5.00	-5.00	25.00	-5.00	88.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00
Bi (0.01ppm)	0.08	0.42	1.60	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	0.08	0.02	0.11	0.02	0.01	0.10	0.01	0.01	0.01
Co (0.1ppm)	49.00	44.20	68.00	67.90	53.70	53.70	81.30	75.60	75.60	44.70	52.70	55.40	62.20	52.20	41.90	38.90	31.00	62.80
Cr (1ppm)	711.00	620.00	1115.00	1000.00	833.00	833.00	1440.00	911.00	911.00	252.00	598.00	123.00	341.00	290.00	110.00	157.00	254.00	195.00
Cu (0.2ppm)	357.00	49.10	7160.00	44.50	270.00	270.00	14.20	6.60	6.60	368.00	13.70	1330.00	8.90	6.70	79.80	10.40	7.70	37.60
Ni (0.2ppm)	935.00	722.00	1425.00	1300.00	1070.00	1070.00	1500.00	1360.00	1360.00	972.00	1065.00	1295.00	1085.00	1020.00	437.00	697.00	683.00	1455.00
Pb (0.2ppm)	48.40	18.70	2120.00	450.00	9590.00	9590.00	13.00	5.40	5.40	416.00	31.20	>10000	6.10	40.30	422.00	13.10	25.60	3.30
Sb (0.05ppm)	137.50	35.10	>1000	53.70	120.00	120.00	18.20	20.20	20.20	115.00	1.51	517.00	1.01	16.75	8.84	0.30	0.17	4.14
Zn (2ppm)	324.00	207.00	1135.00	452.00	273.00	273.00	44.00	21.00	21.00	23.00	359.00	17.00	23.00	30.00	1165.00	45.00	106.00	9.00

Dedection limit for * 0.01 wt.%, ** 5 ppb, LI: Type I Listwaenite, LII: Type II Listwaenite, SPL: spilite, SER: serpentinite, MRB: marble, EGSC: epidote glaucophane schist, CSC: calc-schist, SQSC: serisite quartz schist

Table 2. (continued)
Table 2. (continued)

Rock Type	LII	LII	LII	LII	LII	LI	LII	LI	LII	SPL	SPL	SER	SER	SER	MRB	EGSC	CSC	SQSC
Sample no./ Dedection limit	DO-37	DO-38	KA-39	KA-40	KA-41	KA-44	YA-45	YA-46	BA-48	AT-1	AT-2	AT-3	AT-4	GE-9	AT-11	AT-16	AT-17	AT-18
Rb (0.1ppm)	0.50	0.60	0.90	0.50	0.60	0.30	0.30	1.90	0.90	13.00	23.80	0.40	0.80	0.20	0.50	45.50	9.90	17.80
Th (0.2ppm)	-0.20	-0.20	-0.20	-0.20	-0.20	0.30	-0.20	-0.20	-0.20	1.30	3.10	-0.20	-0.20	-0.20	-0.20	6.40	0.70	5.60
U (0.05ppm)	-0.05	0.17	0.15	0.10	0.16	-0.05	-0.05	0.06	-0.05	0.60	0.70	0.80	-0.10	0.12	1.30	0.90	0.50	0.80
Ta (0.05ppm)	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	1.22	2.85	-0.05	-0.05	-0.01	-0.05	6.62	0.06	0.44
La (0.2ppm)	0.20	0.20	0.20	0.20	0.60	2.20	0.20	0.40	-0.20	15.40	31.60	-0.50	-0.50	2.50	1.00	80.80	4.90	24.10
Ce (0.05ppm)	0.36	0.24	0.34	0.31	0.80	3.97	0.46	0.88	0.18	32.70	65.50	0.68	0.09	4.39	0.86	162.50	6.24	44.80
Sr (0.2ppm)	16.40	142.50	594.00	405.00	381.00	113.00	1180.00	649.00	95.60	422.00	223.00	6.60	4.00	22.70	193.50	188.50	238.00	5.80
Zr (0.5ppm)	-0.50	-0.50	-0.50	-0.50	0.90	-0.50	-0.50	-0.50	-0.50	89.80	146.00	1.90	-0.50	2.20	1.30	123.00	6.90	35.00
Y (0.05ppm)	0.35	0.73	1.19	0.69	1.14	2.21	0.31	2.12	0.30	17.00	16.80	0.80	0.70	1.49	1.80	25.80	5.90	15.90
Hf (0.02ppm)	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	2.80	3.50	-0.10	-0.10	0.03	-0.10	5.20	0.20	1.20
Nb (0.05ppm)	0.09	0.10	0.07	0.08	0.09	0.10	0.13	0.05	0.05	20.40	47.80	0.40	0.10	-0.05	0.20	108.00	1.00	6.40
P (10ppm)	180.00	30.00	10.00	40.00	40.00	350.00	190.00	10.00	40.00	1040.00	1710.00	70.00	30.00	20.00	300.00	3540.00	260.00	940.00
Ti *	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	0.92	0.98	0.02	0.01	0.01	-0.01	2.55	0.02	0.17
Ba (10ppm)	20.00	20.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	60.00	80.00	10.00	-10.00	10.00	10.00	280.00	30.00	70.00
K *	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.06	0.02	0.47	0.88	0.01	0.01	-0.01	0.01	1.32	0.22	0.34
Mn (5ppm)	624.00	682.00	659.00	355.00	538.00	689.00	571.00	632.00	607.00	854.00	1275.00	818.00	916.00	584.00	64.00	1430.00	352.00	852.00
Mo (0.05ppm)	0.35	1.50	0.30	0.25	0.30	0.55	0.39	0.45	0.37	0.48	0.55	0.45	0.44	0.47	0.05	0.71	0.42	0.56
Ca *	0.34	10.45	11.40	16.90	17.70	3.83	13.15	12.30	2.50	12.75	5.79	0.28	0.42	0.36	37.60	5.12	12.25	0.26
Mg *	15.40	5.00	9.52	8.52	6.76	8.46	6.58	6.19	14.40	2.78	2.51	21.80	22.30	17.95	0.24	3.34	0.14	1.22
S*	-0.01	0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	0.01	-0.01	0.01	0.01	0.01	-0.01	-0.01	0.01	-0.01
Ag (0.01ppm)	1.99	0.85	2.34	1.07	0.65	0.06	0.02	-0.01	-0.01	0.05	-0.01	0.06	-0.01	0.01	0.06	0.96	0.06	0.13
As (0.1ppm)	6.40	14.00	9.00	-2.00	13.00	6.80	10.00	16.00	1.10	-5.00	3.40	2.30	0.80	1.00	-5.00	5.80	-5.00	21.90
Au** (5ppb)	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00	-5.00
Bi (0.01ppm)	0.01	-0.01	0.01	0.01	0.01	0.02	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	0.01	-0.01	0.07	0.01	1.36
Co (0.1ppm)	67.90	86.10	53.00	35.10	58.70	33.70	35.90	33.40	66.80	40.30	73.30	102.50	106.00	94.90	1.50	45.70	3.20	15.40
Cr (1ppm)	179.00	845.00	362.00	182.00	221.00	215.00	137.00	751.00	293.00	138.00	348.00	1345.00	1385.00	1290.00	9.00	169.00	10.00	40.00
Cu (0.2ppm)	46.90	20.10	15.90	8.30	16.60	18.50	5.30	5.30	4.90	74.60	79.20	19.00	16.20	9.70	2.10	121.50	12.40	45.80
Ni (0.2ppm)	1600.00	1715.00	1075.00	548.00	1015.00	436.00	326.00	373.00	1415.00	127.50	340.00	2040.00	2140.00	1990.00	10.60	103.50	13.30	47.90
Pb (0.2ppm)	6.60	2.90	11.50	11.80	10.10	2.10	2.20	2.30	0.90	46.40	8.60	39.10	6.70	1.10	6.50	40.10	5.60	26.80
Sb (0.05ppm)	2.74	1.41	0.43	0.29	0.62	0.14	1.78	1.16	0.08	2.67	2.32	20.70	2.69	0.05	1.00	12.55	3.40	16.15
Zn (2ppm)	16.00	14.00	39.00	12.00	12.00	11.00	7.00	11.00	11.00	66.00	110.00	40.00	52.00	35.00	4.00	132.00	14.00	54.00

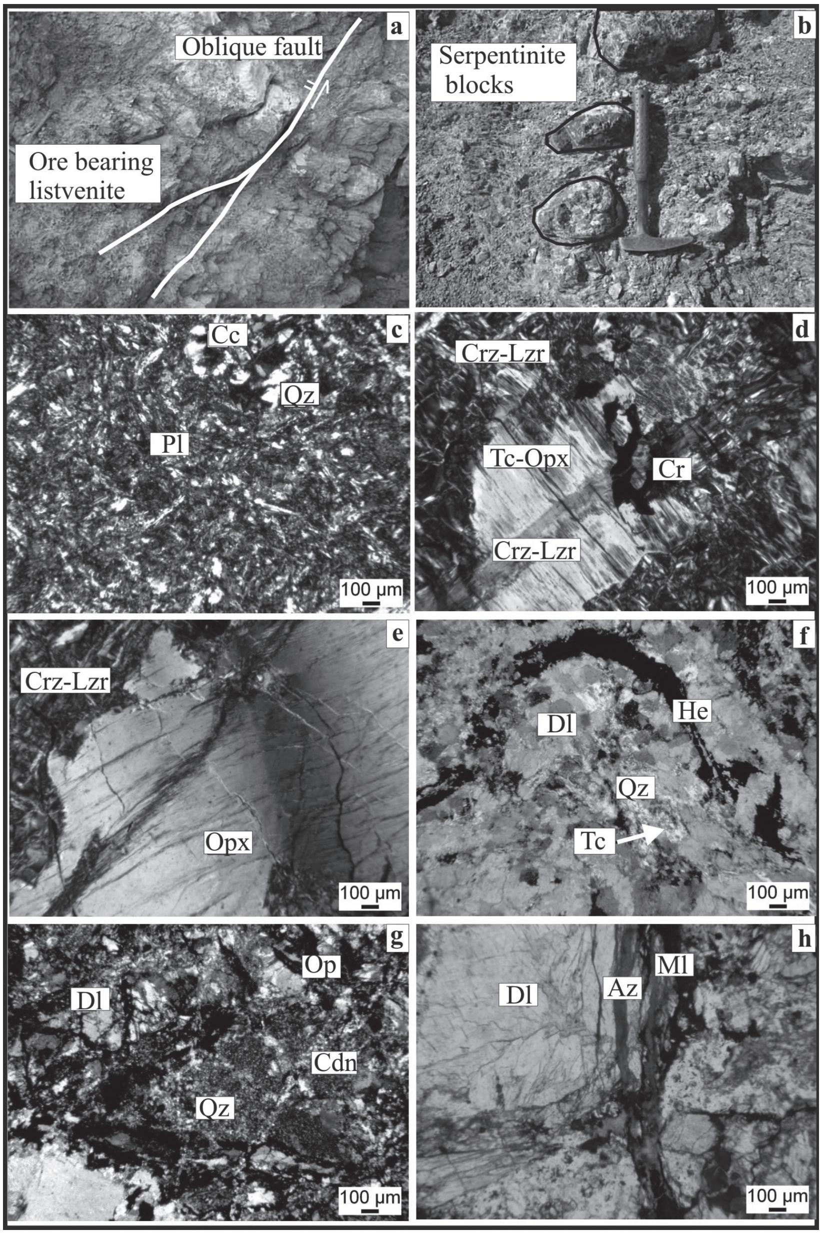


Figure 3. (a, b) macro-photos of ore-bearing listwaenite and serpentinite respectively, (c-h) photomicrographs of spilite and listwaenite (except h, cross-polarized transmitted light) Pl, plagioclase; Qz, quartz; Cc, calcite; Crz, crysotile; Lzr, lizardite, Tc, talc; Opx, ortopyroxene; Cr, chromite; Dl, dolomite; He, hematite; Op, opaque; Cdn, chalcedony; Az, azurite; Ml, malachite. (a) ore-bearing listwaenite (OBL) cut by young oblique fault (b) a typical view of accretionary prism of serpentinite. (c) spilite vuggies are filled by quartz and carbonate minerals (d) orthopyroxene replaced by lizardite and crysotile in chromite bearing serpentinite (e) undulatory extinction of pyroxene due to stress (f) hematite veinlets in listwaenite fractures (g) partly brecciated texture in listwaenite (h) azurite and malachite veinlets in listwaenite fractures.

Şekil 3. (a, b) cevherli listvenit ve serpantinite ait makro fotoğraflar, (c-h) listvenit ve spilitin mikroskop görüntüleri (h hariç, Çift Nikol) Pl, plajyoklaz; Qz, kuvars; Cc, kalsit; Crz, krizotil; Lzr, lizardit, Tc, talk; Opx, ortopiroksen; Cr, kromit; Dl, dolomit; He, hematit; Op, opak; Cdn, kalsedon; Az, azurit; Ml, malakit. (a) cevherli listveniti (OBL) kesen oblik fay (b) serpantinitin tipik bir yığışım prizma görüntüsü (c) spilitin kırıklarını dolduran kuvars ve karbonat mineralleri (d) kromit içeren serpantinitte ortopiroksenin lizardit ve krizotil tarafından ornatılması (e) stres etkisi sonucu piroksende gözlenen dalgalı sönme (f) listvenitin kırıklarını dolduran hematite damarcıkları (g) listvenit gözlenen kısmen breş dokusu (h) listvenitte azurit ve malakit damarcıkları.

are also affected by hydrothermal fluids and they contain secondary carbonate and quartz veins. All units show the presence of shearing effects. It is understood that both shearing and thrust tectonics were effective in the formation of the ore bearing listwaenite (OBL) (Figure 3d). Orthopyroxenes are commonly converted to lizardite and chrysotile. Talc and carbonate minerals are present in the OBL containing relict chromite (see Figure 3d). The pale green lizardite has directly replaced olivine and orthopyroxene. Pressure shadows observed in pyroxenes of the serpentinites indicate the effects of tectonism (Figure 3e).

Marble

The marbles belonging to the Bitlis Massive are imbricated with ophiolitic units. They are generally banded and locally massive form, in different places. In thrust contacts, marble units show a stratification of approximately one meter and exhibit a massive appearance in some places. Both the contact zones along the thrust planes with ophiolites, and the shear zones crossing the units and the young faults have served for passing the hydrothermal fluids for OBL occurrences (see Figure 1).

Transition Rocks

The effects of regional tectonism that resulted in schistic texture are observed both macroscopically and microscopically. In this zone, low grade metamorphic rocks with many different paragenesis can be defined. The transition zone has been described by Yılmaz et al. (1981). In this study, calc-schist, epidote-glaucophane schist and serisite quartz schists are defined petrographically. Intense shearing effects along the E-W direction can be observed throughout this zone. Calc-schists consist of calcite and quartz with trace amounts of muscovite. Epidote-glaucophane schists are mainly formed by quartz, epidote and glaucophane. Glaucophanes are altered to chlorites as a result of retrograde metamorphism. Serisitic quartz schists abundantly consist of quartz. Towards the north, schists show a transition to meta-lava and meta-cherts. Reddish-brown meta-cherts, showing very frequent intercalated with meta-lava, are mostly folded and fractured. All these units should be tectonically controlled and their relations with each other need to be clarifyied.

Listwaenites

Listwaenites are very easily distinguished from other rocks due to their yellow-brown colours and porous textures. In this study, rock samples taken from the listwaenites covering the study area along an E-W direction, are petrographically and geochemically investigated. Listwaenites are mainly composed of dolomite/ankerite quartz, chalcedony, with minor amount of calcite, magnesite, chlorite and fuchsite. Magnetite, pyrite, hematite and chromite are the opaque minerals involved in the listwaenites. The mineralogical compositions of listwaenites change in each sample. For this reason, the listwaenites were classified into two-sub groups based on their SiO_2 contents. Silica-rich listwaenites were named as Type I SiO_2>35.52 %, and carbonate-rich listwaenites were named as Type II (SiO_2≤35.52 wt %). Listwaenite is formed by the development of micro-crystalline cristobalite and macro-crystalline quartz due to the removal of silica from serpentinites. The introduction of silica and other enriched elements such as Au, Ag, Cu, Pb, Sb, As, Rb, Ba, K in OBL indicates an acidic nature of the hydrothermal fluids that were active for the listwaenite formation, as, discussed for the other listwaenites of Turkey by Uçurum (2000) and Akbulut et al. (2006). The listwaenite in the Atalan region is in the form of irregular lenses along the fault zones between ophiolites and marbles (see Figure 2). While the listwaenites are encountered as 35–40 m long and 10–15 m wide small lenses, the listwaenitization observed in the northwest of Șalıgöl village are 700 – 800 m long and 250 m wide. Another listwaenite zone located at the south of Șalıgöl village is approximately 500 m long and 200 m wide (see Figure 2). The difference between the listwaenites in the south of Atalan village from the other listwaenites is the presence of metal enrichment. In thin-section, subhedral dolomite crystals, radially ordered chalcedony fibers and small quartz crystals were the most common components. It also contained late phase quartz and carbonate veinlets. The opaque minerals found were described as limonite and hematite (Figure 3f). Intense cataclastic effects caused the development of occasional brecciated textures (Figure 3g). Malachite and azurite were also easily distinguished macroscopically and microscopically by their distinct colors (Figure 3h). In thin sections, some of the listwaenite samples showed a foliation due to flattening and shearing. Although not every ore zone observed in the listwaenites has been reported, a small exploration gallery was opened by villagers 10 years ago. This study's mineral paragenesis is nevertheless the first such description from this area.

Ore Mineralogy

Tetrahedrite, galena, chalcopyrite, pyrite, millerite, sphalerite, argentite, gold and magnetite were found to form the primary opaque mineral paragenesis in the OBL zones. Covellite, chalcosine, malachite, azurite, anglesite, cerussite, violoarite, bindheimite and limonite were secondary minerals, that resulted from surficial processes due to oxidation. The listwaenite samples taken from the other zone consisted of hematite, magnetite, pyrite and chromite in minor phases. Tetrahedrite was the main opaque mineral in the listwaenites of the OBL zone. Tetrahedrites were observed in the cracks. Argentite (Figure 4a) and native gold were observed as inclusions (25 micron) in the tetrahedrite (Figure 4b). The second most common opaque mineral galena was found to be generally altered to cerussite and anglesite. Tetrahedrite was altered to bindheimite, chalcosine, covellite, azurite and malachite. Galena was younger than the tetrahedrite (Figure 4c). The formation of galena should probably be under lower temperature conditions, after the formation of tetrahedrite which is a high temperature mineral (Ramdohr, 1980). Light yellow millerite was the oldest opaque mineral. The maximum grain size of the millerites was 70 micron and the millerites were mostly observed as inclusions in tetrahedrite, and accompanied by chalcopyrite (Figure 4d). The chalcopyrite was subhedral and unhedral, and its grain size mostly ranged between 5 and110 microns, being found as free grains and connected to sphalerite grains. The sphalerite was accompanied by chalcopyrite (Figure 4e). Violarite was observed only in one polished section. It occurs as alteration product of millerite. Chromite was observed in minor phase compared to serpentinites. The chromite was unhedral and euhedral and it showed a cataclastic texture, especially in the large crystals. Only narrow rims of magnetite had developed at the margins of the chromites and along the fractures (Figure 4f, sample no AT-4). Pyrite grains (10 to 200 μ) as euhedral and subhedral crystals altered to limonite were found along the margins. Magnetite was observed in minor phase in both serpentinites and listwaenites. Malachite and azurite were cross-cut by the veins of quartz and carbonate. The limonite was formed from pyrite and chalcopyrite.

GEOCHEMICAL STUDIES

Major Oxides

The major oxide compositions of specimens from 23 listwaenites, 3 serpentinite, 2 spilite, 1 marble and 3 sample of schists are given in Table 1. Four mineralized samples belonging to the OBL were not analyzed for major oxides (samples no: AT-7, AT-8, AT-9 and AT-10). The major oxide contents of continental crust, MORB and Alpine type peridotites (Table 3) were used for comparing the element variations in listwaenites and serpentinites. Because of their low solubility, MgO, Fe_2O_3, K_2O and CaO are the most variable major oxides that are mobilized during the alteration of serpentinite. Al_2O_3 and Na_2O contents also change in small amounts. According to the geochemical analyses, the listwaenites were depleted in MgO, Fe_2O_3, and Na_2O and enriched in K_2O, CaO, CO_2 and H_2O with respect to average serpentinite. The SiO_2 contents of average listwaenite (n=23, 29.51 % SiO_2) are also depleted with respect to average serpentinites (n=3, 35.52 % SiO_2). Serpentinites in the study area have an average value of 38.24 % MgO content, like other serpentinites in Turkey and in the world (e.g. Brindley and Zusmman, 1957; Wicks and Plant, 1979, Uçurum, 2000, Akbulut et al. 2006). No significant variation was observed in TiO_2 and P_2O_5. MnO increased only in the OBL. Listwaenites were classified in two-sub groups based on SiO_2 content considering major oxide values obtained from chemical analysis. Silica-rich listwaenites were named as Type I, (SiO_2 > 35.52 wt %), carbonate-rich listwaenite were named as Type II, SiO_2 ≤35.52 % (see Table 1). In the SiO_2-Fe_2O_3-CaO+MgO ternary diagram, all samples (serpentinite, listwaenite and marble) fell along the line of SiO_2-CaO+MgO (Figure 5a). The variation of Ni, As and Au in the serpentinite, marble and listwaenites is shown on the Ni-As-Au ternary diagram (Figure 5b). All the samples are plotted along the Ni-As edge of the diagram due to low Au values.

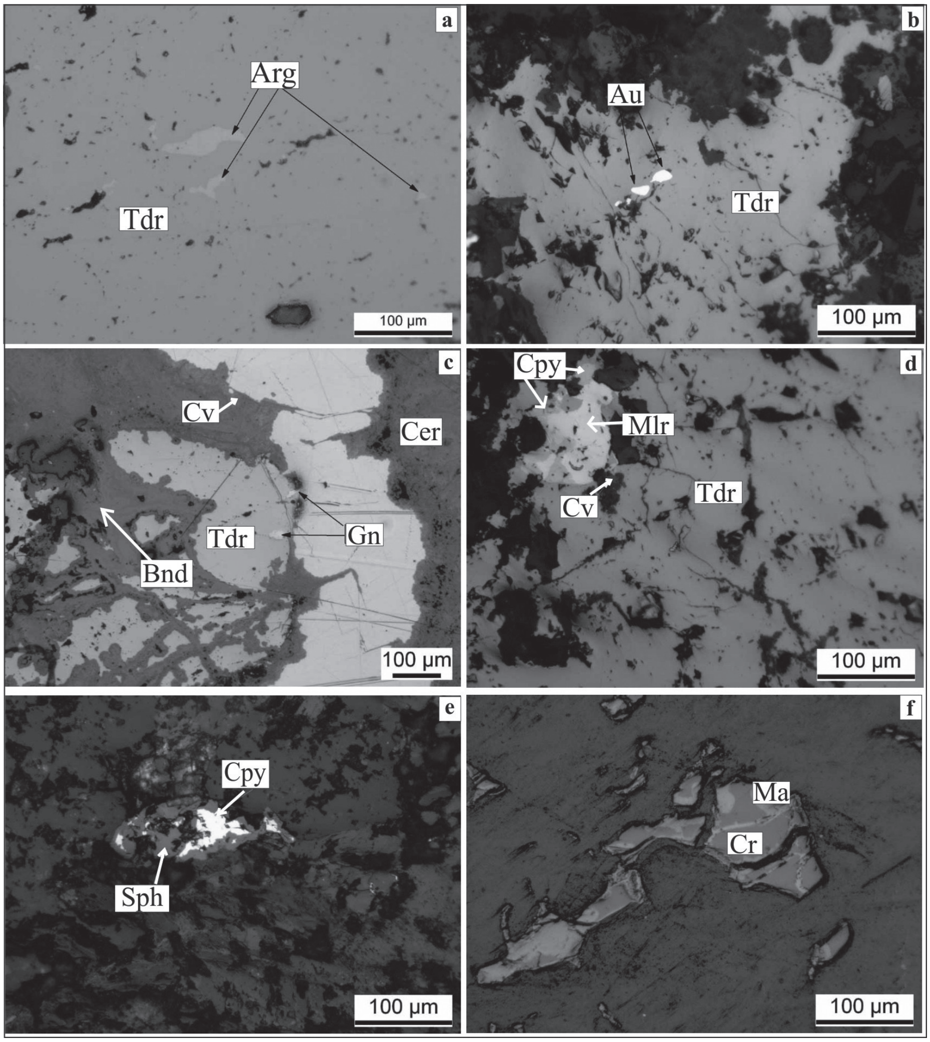


Figure 4. Photomicrographs of ore minerals determined in OBL (all photos are plane-polarized reflected light) (a) argentite (Arg) inclusion in tetrahedrite (Tdr; sample no AT-8), (b) native gold (Au) in tetrahedrite (Tdr) (sample no AT-7), (c) tetrahedrite (Tdr) replaced by galena (Gn), binheimite (Bnd), covellite (Cv) and cerussite (Cer) formed by oxidation processes (sample no AT-9), (d) chalcopyrite (Cpy) replaced to millerite (Mlr) (sample no AT-7), (e) sphalerite (Sph) accompanied with chalcopyrite (Cpy) (sample no AT-8), (f) cataclastic chromite (Cr) replaced by magnetite (Ma) in serpentinite (sample no AT-4).

Şekil 4. Cevherli listvenit içindeki (OBL) cevher mineralleri (tüm fotoğraflar Tek Nikol) (a) tetraedritte (Tdr; örnek no AT-8) arjantit (Arg) kapanımı, (b) tetraedritte (Tdr) damla şekilli nabit altın (Au) (örnek no AT-7), (c) oksidasyon koşullarında galeniti (Gn) ornatan (örnek no AT-9) tetraedritte (Tdr), binheimit (Bnd), kovelin (Cv) ve seruzit (Cer), (d) milleriti (Mlr) ornatan kalkopirit (Cpy) (örnek no AT-7), (e) sfalerit (Sph) ile kenetli kalkopirit (Cpy) (örnek no AT-8), (f) serpantinitte magnetit tarafından ornatılmış (Ma) kataklastik kromit (Cr) (örnek no AT-4).

Table 3. The average values of Alpin Type Peridotites (ATP), MORB and Continental Crust (CC), with average major oxide values of this study listwaenites (TSL) and Serpentinite (TSS) (* Ringwood, 1977 ** Melson et al., 1976; *** Haris, 1972)

Çizelge 3. Ortalama Alpin Tipi Peridotit (ATP), MORB, Kıtasal kabuk (CC) ile bu çalışmadaki listvenitlerin (TSL) ve serpantinitlerin (TSS) ortalama ana oksit değerleri (Ringwood, 1977; ** Melson vd., 1976; *** Haris, 1972).*

Major Oxides	SiO_2	MgO	CaO	K_2O	MnO	Fe_2O_3	Al_2O_3	Na_2O	TiO_2	P_2O_5
ATP*	41.32	49.81	<0.1	0.005	0.11	1.21	…..	0.05	<0.1	……
MORB**	50.8	7.69	11.44	0.17	…..	……	15.6	2.66	1.43	0.12
CC***	61.9	3.1	5.7	2.9	0.1	2.6	15.6	3.1	0.8	0.3
TSL n=23 sample	29.51	16.11	15.43	0.21	0.37	5.64	1	0.3	0.038	0.02
TSS n=3 sample	35.52	38.24	0.51	0.05	0.11	8.85	1.20	0.21	0.03	0.01

Trace Elements

In Table 2, the trace element results of all the listwaenite and wall rock samples are presented. By considering the chemical analysis, the results of the samples show that the Atalan (Gevaş) area contains an anomaly significant in terms of mineralization. In Table 4, the average value of certain elements (Cu, Zn, Pb, Cr, Ni, Co, Mo, Ag and Au) of listwaenite, spilite, serpentinite and marble are presented. The values of the trace elements obtained from this study, except for those of Cr, are in accord with the Clark value of mafic-ultramafic and limestone (see Table 4). The average Cr value of 1330 ppm given for the serpentinites in this study is lower than the 2000 ppm Clark value of ultramafic rocks (see Table 4).

The Cr value in the listwaenites of the Eskişehir-Mihalıççık (Akbulut et al., 2006), Sivas-Alacahan (Boztuğ et al., 1994) and Malatya-Hekimhan (Uçurum, 2000) regions is higher than the Cr in both the serpentinites and the listwaenites in this study. On the other hand, the average Ni content of the Malatya-Hekimhan region is 718 ppm and 1384 ppm in listwaenite and serpentinites, respectively. (Uçurum, 2000). In this study the average Ni content was 1000 ppm and 2056 ppm in listwaenites and serpentinites, respectively. This value is also higher than that of the Eskişehir-Mihalıççık area (Akbulut et al., 2006). The netal elements increase from non-mineralized listwaenite (NML) to OBL (see Table 2, Figure 6a). The trace elements contents of the listwaenites varied as follows; Co from 9.1 to 86.1 ppm, Ni from 97.8 to 1715 ppm and Cr from 19 to 1440 ppm. Ni and Co were the highest compatible element couple. The Ni/Co ratio was approximately 20 in all of the listwaenites and serpentinites samples. The lowest Ni, Co and Cr values were obtained from the carbonate-rich listwaenite sample (sample no AT-15) only. This situation indicates that the amounts of Ni, Co and Cr decrease in carbonate-rich listwaenite (see Table 2; Figure 6b). The Ni/Co ratios for mafic-ultramafic rocks given in Table 4 are also consistent with those obtained from listwaenites, serpentinites and spilites in this study (see Table 2).

An anomalous gold value was found only in the listwaenites of the Atalan area. with maximum values of 0.267 ppm. In all samples taken from other regions, the gold value was lower than detection limits (<5ppb). The value of Au in the primary mantle is 1 ppb (Brugmann et al., 1987), while it is 5 ppb in the serpentinized ultramafic (Buisson and Leblanc, 1986). The highest gold value obtained was 267 ppb Au in sample AT-7; that means 267 times greater than the values for the primary mantle and approximately 53 times greater than the serpentinized ultramafics. The same sample contained 176 ppm Ag, 7160 ppm Cu, 483 ppm As, 1115 ppm Cr, 1425 ppm Ni, 68 ppm Co, 2120 ppm Pb and 1135 ppm Zn. The other samples which had higher gold values with respect to the serpentinized ultramafics were enriched 18 times in sample AT-26, 16

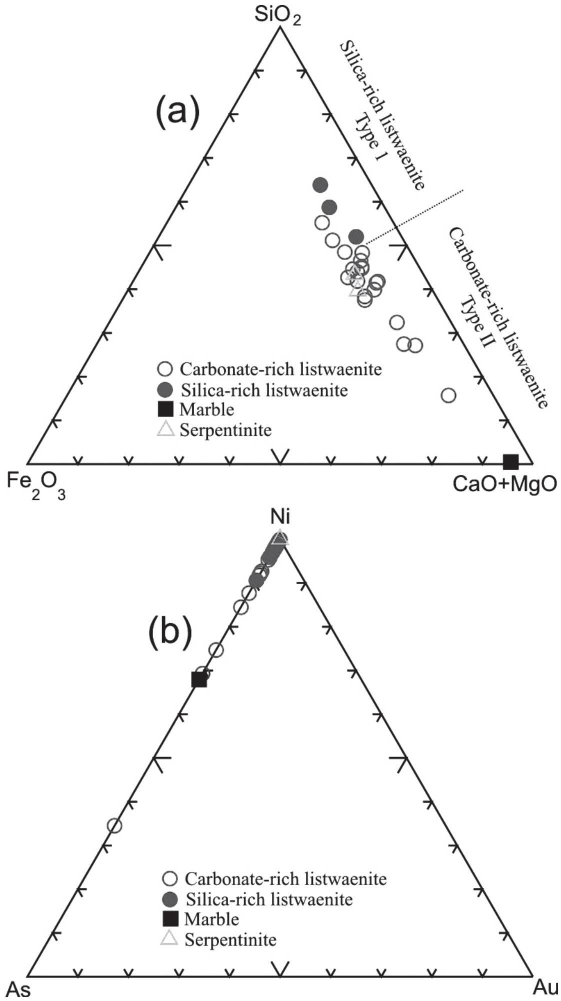


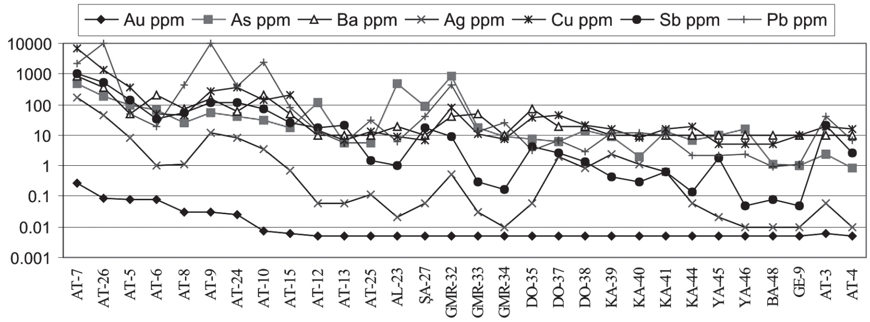
Figure 5. (a) Plotting of listwaenites, serpentinite and marble in SiO_2-Fe_2O_3-CaO+MgO ternary diagram, (b) Ni-As-Au ternary diagram of listwaenite, serpentinite and marble in the study area.

Şekil 5. (a) Listvenit, serpantinit ve mermer örneklerinin SiO_2-Fe_2O_3-CaO+MgO üçgen diyagramındaki dağılımı (b) aynı örneklerin Ni-As-Au dağılımı.

times in AT-5, 15 times in AT-6, and 5 times in AT-24 (see Table 2). While there were no Au anomalies found outside of the Atalan area, Ag values showed up as anomalous in some listwaenite samples. While the highest Ag value (176 ppm) was found in the same sample as that with the highest Au value (267 ppm), the Ag anomaly around Kayalar village was 2.34 ppm (sample no KA-39). The lack of correlation of Pb with Au and Ag is also consistent with the ore microscopy studies, since no sulphosalt mineral was identified in the galenas. The Ag values of Dokuzağaç and the Kayalar area (see Figure 1) are presented in Table 2 as 1.99 ppm, 0.85 ppm, 2.34 ppm and 1.07 ppm. The Pb values of these samples did not give rise to any anomalies. Similarly, a Ag value of 0.96 ppm was found in the epidote glaucophane schist, which is a transition zone rock and does not contain other metals. The As content of the listwaenites within the Atalan area varied from 5.6 ppm to 483 ppm. The maximum As content was found as 822 ppm in sample GR-32. The lowest trace element contents were found in the serpentinites. While, within the listwaenites that formed as a result of the alteration of serpentinites the amount of Ni, Co and Cr was depleted in the same ratio, the listwaenites were enriched in Au, Ag, Cu, Pb, Sb, As, Rb, Ba, K and Zn elements with different ratios (Figure 6b). This suggests that hydrothermal fluids were introduced into those elements during the formation of the listwaenites. The Sb value of the samples varied from 0.14 ppm to an uncertain value over 1000 ppm. The highest Sb value was again obtained in sample AT-7, which showed the highest Au value. An Sb value greater than 1000 ppm was due to the presence of tetrahedrite. The Zn content varied from 17 to 1135 ppm in the Atalan area. The highest Zn value of 1165 ppm was obtained from sample GR-32. Zn showed a weak anomaly with highest 1165 ppm in geochemical results compared to other metals. Pb showed high values only in the listwaenite samples of the Atalan area. The highest Pb values were 9590 ppm (sample no AT-9) and over 1 % (sample no AT-26). Cu and Ba values were 7160 ppm and 870 ppm in AT-7 and 1330 ppm and 350 ppm in AT-26, respectively.

There exists a positive correlation for the Au and Ag elements with the Sb, Cu, Ba and As values. The correlation coefficient, ($r > 0.93$) is relatively high (Figures 7 and 8). On the other hand, correlation coefficients for Ag and Au with Pb, Ni and Zn are low (i.e. the correlation coefficients for Ag with Pb, Ni, and Zn are

(a)



(b)

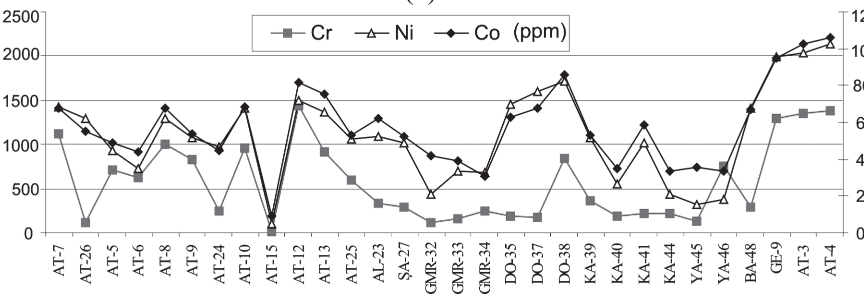


Figure 6. (a) Trace element distributions in all listwaenite (n=27) and serpentinite (n=3) samples for Au, As, Ba, Ag, Cu, Sb, Pb elements (b) Co, Ni, Cr element distributions in the same samples (Listwaenites:AT7-BA48 and Serpentinite (SER): GE-9, AT-3 and AT-4 samples (Co values have been shown in the second axes).

Şekil 6. (a) Listvenit (n=27) ve serpantinit (n=3) örneklerinin Au, As, Ba, Ag, Cu, Sb, Pb element dağılımarı (B) aynı örneklerdeki Co, Ni ve Cr dağılımları (Listvenit AT7- A48; Serpantinit (SER), GE-9, AT-3 ve AT-4 nolu örnekler (Co değerleri ikinci eksende gösterilmiştir).

Table 4. Average mean values of some elements in ultramafic, mafic and limestone (Krauskopf, 1979; Rose et al., 1979; *Turekian, 1977).

*Çizelge 4. Ultramafik, mafik ve kireçtaşında bazı elementlerin ortalama bulunma miktarları (Krauskopf, 1979; Rose et al., 1979; *Turekian, 1977).*

Rock Type/ Element	Cu ppm	Zn ppm	Pb ppm	Cr ppm	Ni ppm	Co ppm	Mo ppm	Ag* ppm	Au*
Ultramafic rocks	42	58	1	2000	2000	110	0.3	0.06	0.0032
Mafic Rocks	72	94	4	300	130	48	1.5	….	….
Limestone	5	21	5	5	20	0.1	0.4	….	….

Table 5. Some trace and rare earth element analyses from selected samples AT-7 (OBL); DO-38 (NML) and average values of serpentinite (TSS).

Çizelge 5.Sahayı karakterize eden temsili örneklerin iz ve nadir toprak element (REE) dağılımları AT-7 (cevherli listvenit);DO-38 (cevhersiz listvenit) ve ortalama serpantinit (TSS).

	Element (all in ppm)													
Rock Type	K	Nb	P	Hf	Ti	Rb	Ba	Th	U	Ta	La	Ce	Sr	Zr	Y
TSS	100	0.25	40	0.03	140	0.46	10	0.2	0.46	0.01	2.5	1.72	11.1	2.05	0.99
AT-7 (OBL)	4900	0.2	10	0.02	120	62	870	0.2	0.3	0.01	0.5	0.32	105	0.8	1.3
DO-38 (NML)	100	0.1	30	0.02	50	0.6	20	0.2	0.17	0.01	0.2	0.24	142	0.5	0.73

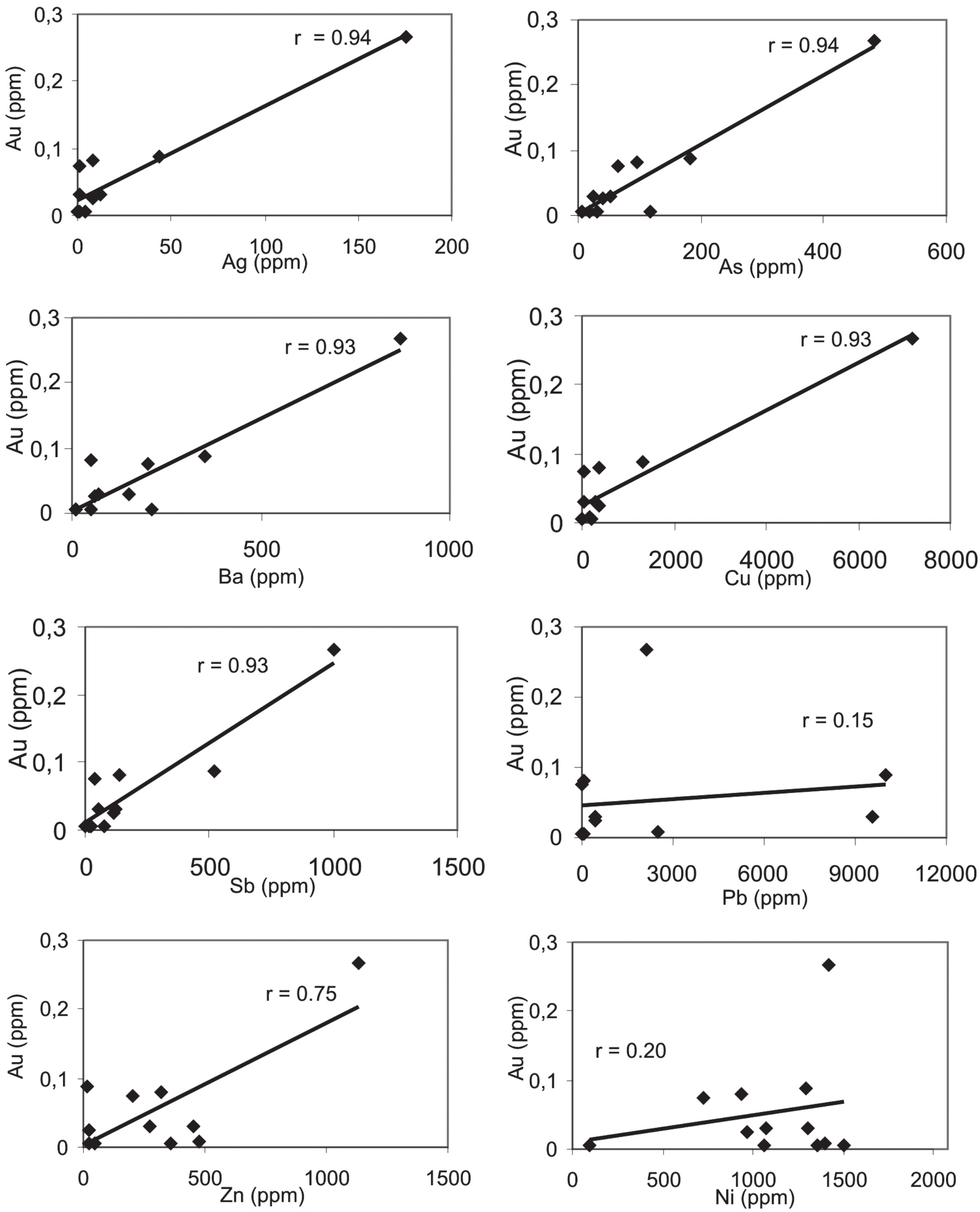


Figure 7. Correlations of Au element with Ag, As, Ba, Cu, Sb, Pb, Zn and Ni.
Şekil 7. Au elementinin Ag, As, Ba, Cu, Sb, Pb, Zn ve Ni ile korelasyonları.

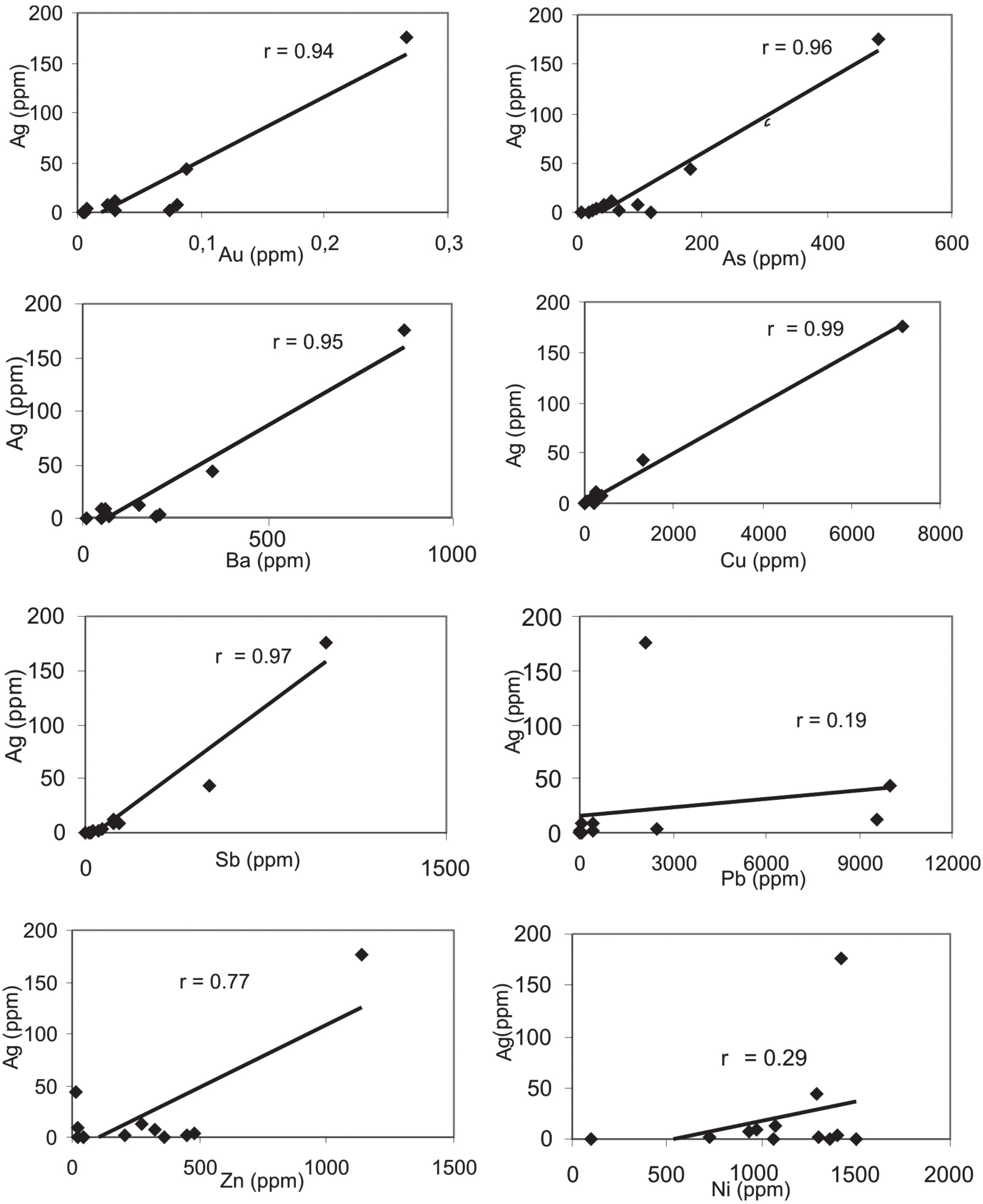


Figure 8. Correlations of Ag element with Au, As, Ba, Cu, Sb, Pb, Zn and Ni.
Şekil 8. Ag elementinin Au, As, Ba, Cu, Sb, Pb, Zn ve Ni ile korelasyonları.

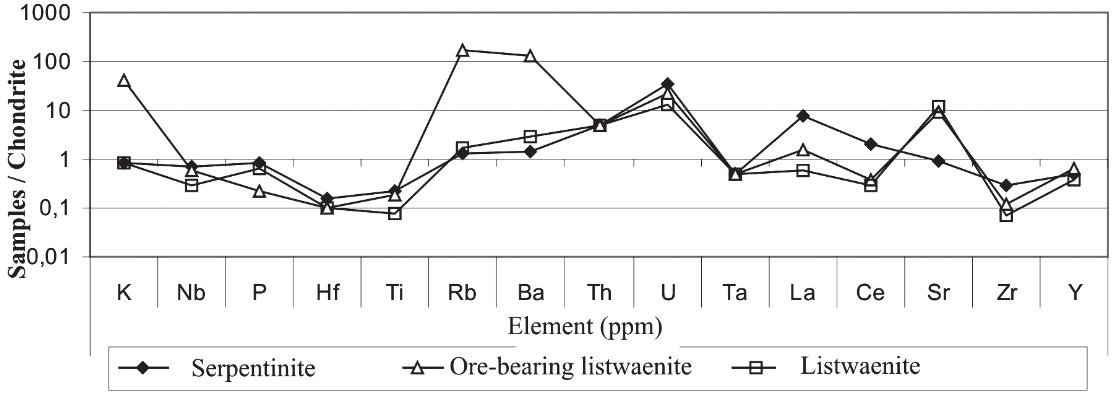


Figure 9. Some trace and rare earth element (REE) pattern normalized to chondrite from selected samples, TSS:average values of this study listwaenite, AT-7 (OBL) and DO-38(NML) samples normalized to chondrite.

Şekil 9. Bazı iz ve nadir toprak elementlerinin (NTE) ortalama serpantinit (TSS), temsili cevher içeren AT-7 no.lu örnek (OBL) ve cevher içermeyen DO-38 no.lu örneklerinin (NML) kondirite gore normalize edilmiş dağılımları.

0.19, 0.29, 0.77, respectively, whereas those for Au with Pb, Ni and Zn are 0.15, 0.20, 0.75, respectively see Figure 7 and 8). The values of the ore-bearing listwaenite (OBL; sample AT-7), non-mineralizing listwaenite (NML; sample DO-38) and mean serpentinite values (n=3) were the best samples representing the region that are selected and presented in Table 5. The distribution of the elements in serpentinite, OBL and NML, normalized to chondrite has been plotted (Figure 9).

In the trace element distribution of serpentinites with respect to chondrite, no change was observed in the Sr element. While K, Nb, P, Ta and Y showed some amount of depletion, Hf, Ti and Zr showed depletion up to 10 times. While Rb, Ba and Ce showed some amount of enrichment, with Th and La this went up to 10 times and U showed a 50 times enrichment (see Figure 9). The trace element diagram of OBL, normalized with respect to chondrite Nb, Ta, Ce, P and Y, showed some amount of depletion, while, Hf, Ti and Zr showed up to 10 times depletion. Some amount of enrichment was observed in La, while up to 10 times enrichment in Th and Sr, 50 times enrichment in K and U, 100 times enrichment in Rb and Ba were observed (see Figure 9). In the trace element distribution of listwaenites, normalized with respect to chondrite, K, Nb, P, Ta, La, Ce and Y showed some amount of depletion and Hf, Ti and Zr showed up to 10 times depletion. While some amount of enrichment in Rb and Ba, up to 10 times enrichment in Th, U and Sr was observed (see Figure 9). All values are summarized in Table 6. With respect to chondirite normalization, all the rocks of this group were enriched in U, Th, Ba and Rb elements. While Sr was enriched in all listwaenite types, K was enriched in OBL when compared to serpentinite (see Table 6).

DISCUSSION

The mineral paragenesis and the Cr, Ni, and Co values of Gevaş listwaenites are similar to those of listwaenites defined by previous researchers (Buisson and Leblanc, 1985; Auclair et al., 1993; Halls and Zhao, 1995, Uçurum, 2000). The presence of fuchsite, Ni and Cr values of approximately 1000 ppm, and also the presence of K are consistent with the listwaenite rock definitions of recent history (Rose, 1837; Abovian, 1978; Halls and Zhao, 1995). Studies carried out all around the world and in Turkey have revealed that the precious metal contents of the most

Table 6. Trace element distribution of serpentinite, Ore-bearing listwaenite (OBL) and listwaenite respect to chondrite. (s) some amount, (-) depletion, (+) enrichment, number (10) times.
Çizelge 6. Serpantinite, OBL (cevherli listvenit) ve listvenite ait bazı iz elementlerin kondirite göre dağılımı. (s) az miktar, (-) fakirleşme, (+) zenginleşme (örneğin 10 kat).

	Elements														
Element/ Rock	K	Nb	P	Hf	Ti	Rb	Ba	Th	U	Ta	La	Ce	Sr	Zr	Y
Serpentinite	S (-)	S (-)	S (-)	10 (-)	10 (-)	S (+)	S (+)	10 (+)	50 (+)	S (-)	10 (+)	S (+)	nc	10 (-)	S (-)
OBL	50 (+)	S (-)	S (-)	10 (-)	10 (-)	100 (+)	100 (+)	10 (+)	50 (+)	S (-)	S (+)	S (-)	10 (+)	10 (-)	S (-)
Listwaenite	S (-)	S (-)	S (-)	10 (-)	10 (-)	S (+)	S (+)	10 (+)	10 (+)	S (-)	S (-)	S (-)	10 (+)	10 (-)	S (-)

listwaenites are low and they are not important economically. On the other hand, several gold bearing listwaenites from the upper Proterozoic (Morocco, Saudia Arabia) and Alpine ophiolite complexes contain gold between 1 to 10 ppm (Buisson and Leblanc, 1985). The listwaenites in different regions other than that analysed here have been studied with respect to precious, base metal and trace element contents. The metal paragenesis (Au, Ag, Pb, Sb, and Cu) of Gevaş listwaenites is partially different from many of the other known listwaenites in Turkey, particularly with their high Pb content. But other Pb containing listwaenites (11800 ppm Pb) are known in Sivas-Alacahan (Boztuğ et. al., 1994). These listwaenites have high Co, Ni, and As and low Au contents, compared to the listwaenites investigated in this study. The Gevaş listwaenites have relatively lower values of As and Cr, and higher values of Ni compared to the silica-carbonate listwaenites of Eskişehir-Mihallıççık (Akbulut et al., 2006). The average Cr content of the Malatya-Hekimhan area silica-carbonate type listwaenites and serpentinite are 1861 ppm and 2803 ppm respectively (Uçurum, 2000). In this study, the average Cr content of listwaenites and serpentinite are approximately 485 ppm and 1340 ppm, respectively, lower than the Malatya-Hekimhan region. But the Ni contents show an opposite trend. While the average Ni content found in this study is 1000 ppm in listwaenites and 2056 ppm in serpentinites, these are higher than the Malatya-Hekimhan region, which has 718 ppm and 1384 ppm in listwaenite and serpentinite, respectively. Among these, the Ni/Co ratio has not been changed and it is approximately 20 times enriched both in serpentinites and in listwaenites derived from serpentinized peridotites. In this study, the Co, Cr and Ni values of all listwaenites are lower than those of the limited number of analyzed serpentinites. However, a number of listwaenite samples taken from the Malatya-Hekimhan area have higher Co, Cr and Ni values than the average of the serpentinite samples (Uçurum, 2000). Carbonate rich listwaenites in the study area (sample AT-15) are depleted in Ni, Cr and Co content. These results are consistent with the results obtained from the Moroccan listwaenites (Buisson and Leblanc, 1985). In various studies it has been pointed out that gold enrichment is related to the introduction of silica (Buisson and Leblanc, 1985; Auclair et al., 1993; Halls and Zhao, 1995; Uçurum, 2000; Akbulut et al., 2006). In this study, the gold increases in relation to the SiO_2 content. This is also consistent with the high quartz ratio observed in the thin-sections and Au contain sample from the Atalan area. Au and sulphide complexes might be derived from ultramafic lithologies in a manner similar to that described by Buisson and Leblanc (1986) and Uçurum, (2000). Similarly, it is argued that the Ni, Co, Pb, As, Ba, Zn, Ag, Au, Sb, and Hg metals in the silica carbonate listwaenites of the Malatya-

Hekimhan are enriched with the introduction of Si into the hydrothermal solutions derived from ophiolites (Uçurum 2000; Buisson and Leblanc, 1985, 1986). Silica-carbonate listwaenites are formed by meteoric hydrothermal fluids' influx of SiO_2, CaO, H_2O and Ca, and in lower temperatures (150-300 °C, Uçurum, 2000; <300° Buisson and Leblanc, 1985, 1986). The silica carbonate listwaenites of this study should have been formed probably at temperatures of <300° C. It is advocated that the model of base and precious metal containing listwaenites of East Central Anatolia is applicable to all the listwaenite formations in Turkey (Uçurum, 2000).

When these study results are compared with those from other region's listwaenites, it is seen that in terms of metal enrichment and metal types, there could be some variations. These variations depend on local lithological factors, the presence of discontinuities such as shearing and thrust planes, where solutions could flow, and the duration of fluid-wall-rock interaction. In this study, the presence of a high Pb content in the listwaenite zone, besides Au, Ag, Sb and Cu enrichment, reflects the polymetallic character of the ore-bearing listwaenites (OBL). Enrichment of K, Rb, Ba, Sr, Ti, P and U in OBL, beside a content of 1 wt % Pb, indicates that the source of these elements of continental crustal origin could not be derived from ophiolites alone. In spite of the fact that there are no magmatic intrusions observed on the surface, these elements could be derived from either a magmatic process or the rocks of the Bitlis Massive that have metamorphic origins.

CONCLUSIONS

The Gevaş ophiolite related listwaenite zones occur in serpentinitized peridotite. Mineralogical and geochemical studies have revealed that the base and precious metal contents of listwaenites are enriched in well developed shearing, thrust and fault zones. The accompaniment of the metals within the carbonatized and silicified alteration zone is composed of dolomite/ankerite quartz, chalcedony, with smaller amounts of calcite and fuchsite. A gold anomaly was obtained only from the Atalan area listwaenites, but a silver anomaly was detected up to 2.34 ppm in wall-rocks and in listwaenite from which the gold anomaliy was absent. Listwaenites formed from serpentinites are depleted in MgO, Fe_2O_3, and Na_2O and enriched in K_2O, CaO, and H_2O. The Cr, Ni and Co content of listwaenites are depleted according to serpentinite, but enriched in Au, Ag, Cu, Zn, Sb, As, K, Rb, Sr, Ba, Ti, P, U and Pb contents. A strong positive correlation between Au-As-K and trace elements such as Ba, Cu, Sb, and Ag may also be associated with Au values, and suggests that these elements can be used as indicators of ore zones. The limited number of analyses indicates that the Au value of Gevaş listwaenites is 53 times enriched compared with that of the serpentinized peridotites. Ag, Sb, Pb and Cu are the other enrichment metals. Ag was detected not only in the listwaenite zone but also in shearing zones that are potentially suitable areas for the development of precious metals formed under low temperatures. These geochemical data indicate that detailed and numerous samplings should also be made in the vicinity of thrust faults and shearing zones.

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