Tr. J. of Earth Sciences
7 (1998) 87-95

Application of the Correspondence-Type Geostatistical Analysis on the Co, Ni, As, Ag and Au Concentrations of the Listwaenites from Serpentinites in the Divriği and Kuluncak Ophiolitic Mélanges

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Received: 02.02.1998

Abstract: The main aim of this research was to find out correlation—if there is any-among Co, Ni, As, Ag and Au concentrations in three different listwaenite sampling sets in Diviriği and Hekimhan areas. The low temperature hydrothermal alteration of serpentinite bodies from the Divriği and Kuluncak ophiolitic mélanges in the Cürek, Divriği-Sivas, Güvenç and Karakuz areas, Hekimhan-Malatya, has formed two distinct types of listwaenite. Type I, is silica-carbonate listwaenite, which is dominated by silica+calcite+dolomite+ankerite±magnesite. Type II listwaenite bodies are carbonate listwaenite characterized by calcite+dolomite+ankerite ±magnesite, and lack any significant introduced silica.

Correspondence-type geostatistical analysis has been thought to be the best approach to see possible correlation between Co-Ni-As-Ag and Au. Data sets are obtained from three different sampling sites, and have five attributes. Total number of individuals in three sampling sites is 96. Plots from correspondence analysis of listwaenites' data set developed using the four significant factor–based on the four significant eigenvectors.

Divriği ve Kuluncak Ofiyolitik Mélanjları İçerisindeki Serpantinitlerden Gelişen Listvenitlerin Co, Ni, As, Ag ve Au Konsantrasyonlarında Correspondence-Tip Jeoistatistiksel Analizin Uygulanması

Özet: Bu çalışma Divriği ve Hekimhan bölgelerindeki üç farklı listvenit mostrasından alınan örneklerin Co, Ni, As, Ag ve Au konsantrasyonları arasındaki olası ilişkiyi bulmayı amaçlamıştır. Cürek-Divriği, Sivas , Güvenç ve Karakuz-Hekimhan, Malatya bölgelerinde yer alan Divriği ve Kuluncak ofiyolitik mélanjları içerisindeki serpantinitlerin düşük dereceli hidrotermal çözeltiler ile alterasyona uğramaları sonucu iki farklı tip de lisvenit oluşmuştur. I. Tip lisvenit silika-karbonat lisvenitdir ve ana mineraller silika+kalsit+dolomit+ankerit±manyezit dir. II. Tip lisvenit kütlesi ise karbonat lisvenitdir ve önemli silika getirimi olmaksızın kalsit+dolomit+ankerit±manyezit tarafından karekterize edilmektedir.

Co-Ni-As-Ag ve Au arasındaki olası korelasyonu/ilişkiyi görebilmek için en iyi yaklaşımın Correspondence-tip jeoistatiksel analizinin olduğu düşünülmüştür. Veriler üç farklı örnekleme bölgesinden elde edilmiştir ve 5 farklı bileşime (Co, Ni, As, Ag, Au) sahiptir. Üç farklı örnekleme bölgesinden alınan örneklerin toplam sayısı 96 dır. Listvenitlerin correspondence analiz sonuçlarının yerleştirilmesi için veri seti geliştirilmiştir ki bunlar dört önemli eigenvektör'e dayalı oluşturulan dört önemli faktördür.

Geological Setting

The study has been completed in three distinctive areas in the Taurides tectonic belt of central Anatolia, Turkey (Figure 1A). The Cürek-Divriği (Sivas) area is located about 10 km northwest of Divriği in Sivas province (Figure 1B). The area of investigation is exposed west, northwest and northeast of Cürek village and covers a 9 km^2 area. The Güvenç-Hekimhan (Malatya) area is located about 5 km northeast of Hekimhan in Malatya province (Figure 1C). This study area covers about 21 km^2 area. The Karakuz-Hekimhan area is located at about 17 km northwest of Hekimhan in Malatya province (Figure 1D). The study area is about 13.5 km^2 and is north of Maksutlar village and southwest of Ciritbelen village.

The three areas that were studied occur in two different ophiolitic mélanges within the Taurides tectonic belt (Figure 1A). These are the Divriği ophiolitic mélange (Tunç et al., 1991) in Sivas, and the Kuluncak ophiolitic mélange (Yılmaz et al., 1991) in Hekimhan-Malatya. Both mélanges are late Cretaceous in emplacement age.

The stratigraphic sequence in the Divriği ophiolitic mélange (Figure 1B) from bottom to top is, late Jurassic-early Cretaceous Akdağ limestone, late Cretaceous Çaltı ultramafic rocks, and the Cürek listwaenite. The Divriği ophiolitic mélange is intruded by the late Cretaceous (Michard et al., 1984; Şengör and Yılmaz , 1981; Şengör, 1984; Robertson and Dixon, 1984; Koşal, 1973; Tunç et al., 1991; Boztuğ et al., 1997) or early Cretaceous (Zeck and Ünlü, 1987, 1988a, 1988b) Murmano pluton. The above stratigraphic sequence is followed by the Eocene-Paleocene Ekinbaşı metasomatite and the Quaternary Kilise Formation.

The oldest sequence of rocks in Kuluncak ophiolitic mélange in the Güvenç area (Figure 1C) is the Karadere serpentine/ultramafic and is overlain by the Kurtali gabbro, Gündeğcikdere radiolarite, Güvenç listwaenites, and the Buldudere Formation. All of the above units are late Cretaceous in age. The Karamağra siderite deposit in the Hekimhan area was probably formed in the late Cretaceous at the contact between Çaltı ultramafic rocks and the Buldudere Formation. The Kuluncak ophiolitic mélange was intruded by a sub volcanic trachyte in the late Cretaceous (Uçurum, 1996). The Eocene-Paleocene Konukdere metasomatite, the Miocene Yamadağ volcanic rocks, and Quaternary slope deposits are late in the stratigraphic sequence in the Güvenç area.

The Kuluncak ophiolitic mélange in the Karakuz area (Figure 1D) is similar to that at Güvenç, however, gabbro, radiolarite and Miocene volcanic rocks are not present. The Miocene is represented by the Ciritbelen Formation at Karakuz and the Karakuz iron deposit is hosted by a late Cretaceous sub volcanic trachyte.

Listwaenite was first reported in the study area by Legros (1969) near the iron mines at Divriği. Sezer (1972), Koşal (1973), and Tunç et al., (1991), have since described these same silica-carbonate occurrences as laterite instead of listwaenite. Güvenç listwaenites were first described by Yılmaz (1991) in the Hekimhan area. The Karakuz listwaenite was recognized by Uçurum et al., (1994) and described by Uçurum and Larson (1995). The first detailed listwaenite description and interpretation of the Divriği and Kuluncak ophiolitic mélange in the Divriği-Hekimhan area is described by Uçurum (1996).

Listwaenitic alteration of serpentinite is recognized to form two different rock types which differ one from the other in their mineralogy, chemical composition, stratigraphic position, and the timing of their formation. In this work It has bee termed the earliest formed listwaenite as type I and the youngest listwaenite as type II. Listwaenites are present as both type I (silica-carbonate listwaenite) and type II (carbonate listwaenite) in the Güvenç (Figure 1C) and Karakuz (Figure 1D) areas in the Kuluncak ophiolitic mélange, whereas, in the Cürek area (Figure 1B) of the Divriği ophiolitic mélange only type I is present. Most type I listwaenite occurs as veins along the thrust fault zones which borders the ophiolitic block within the ophiolitic mélange. Type II listwaenite is formed by non-fault related processes at Güvenç, however at Karakuz both type I and type II listwaenite form along thrust fault zones.

Correspondense Analysis

Ninety six samples of Type I and II listwaenites from Cürek-Divriği, Sivas and Güvenç, Karakuz-Hekimhan, Malatya were chemically analyzed to determine their Co, Ni, As, Ag and Au concentrations. All of the analyses were completed at ACTLAB, Ontario-CANADA by use of instrumental neutron activation analysis (INAA) and inductively coupled plasma spectrometry (ICP). Cobalt, Ni, As, Ag and Au concentrations of listwaenites are presented in Table 1A.

The correspondence analysis has been thought to be the best approach to see possible correlation between Co-Ni-As-Ag and Au from listwaenite samples in the central east Anatolia. Correspondence analysis is one of the multivariate data analysis method, which yields simultaneous R-mode and Q-mode analyses. In R-mode analysis a determination is made regarding how the M attributes characterizing N individuals are interrelated. However, Q-mode analysis is used to assess how individual samples are interrelated. Correspondence analysis renders plots showing relative similarity among attributes and individuals, hence simultaneous R- and Q-mode analysis. FORTRAN programs for correspondence analysis are given in David et al., (1977) and in Carr (1990). The book by Greenacre (1984) is entirely devoted to the theory and application of correspondence analysis. A computer program in FORTRAN by Carr (1995, p. 138-145) has been used in this study. Detailed information for application of the Correspondence analysis is available in the book by Carr (1995).

Factors and eigenvalue results (Table 1) may suggest the following:

1. Au is not associated closely with any listwaenite samples in three sampling sites, except in Figures 2, 3, and 4, there is a weak association.

2. Attributes like Ni, Co, and As are closely associated each other in all the plots (Figure 2 through 7) but, correlation in Figure 1 is weak.

3. Many of individuals are closely associated with each other (Figures 2 and 5).

4. Some of the individuals in all three sampling sites are not consistently associated with any attributes.

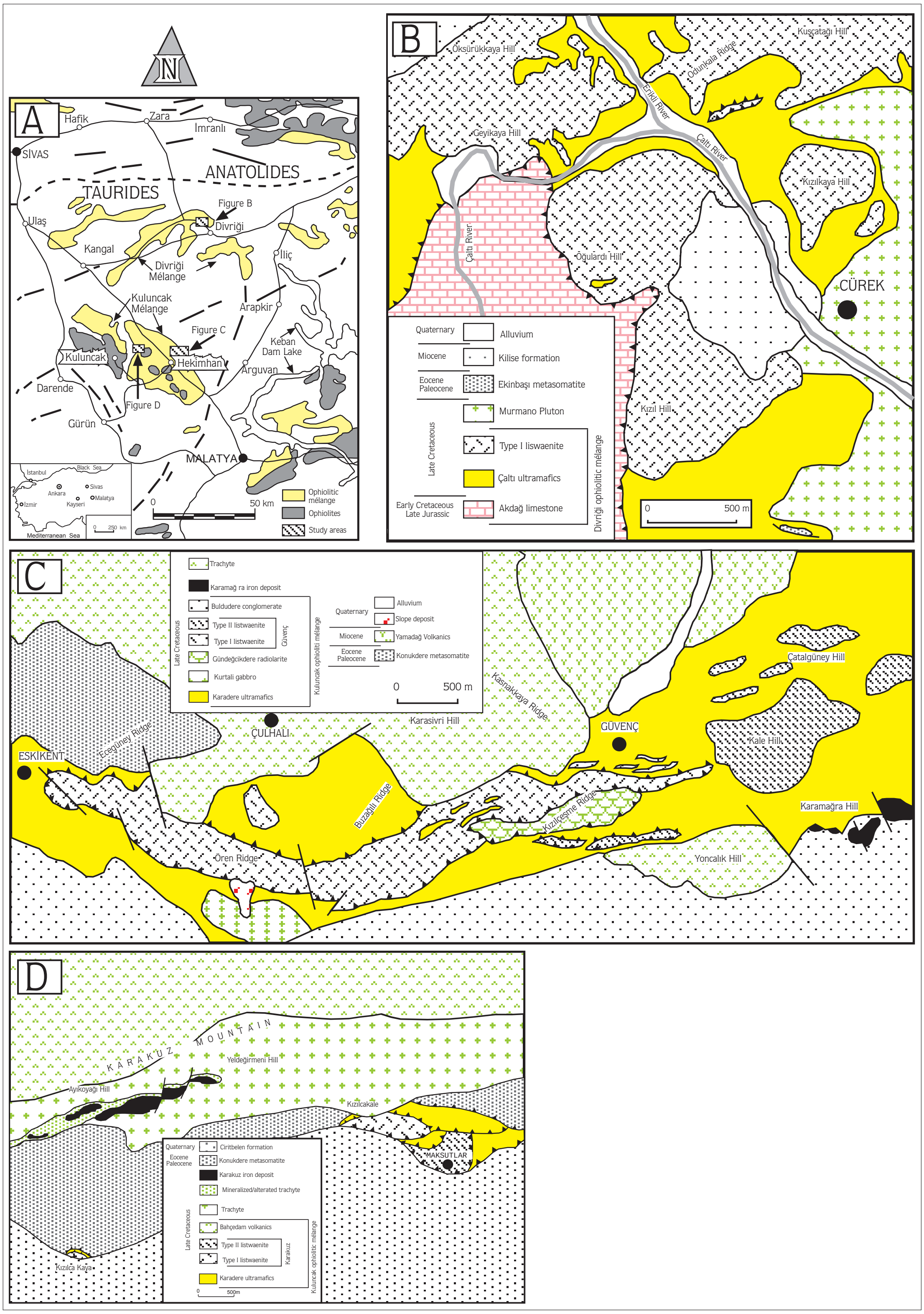

Figure 1. (A) Location map of the study area and distribution of the late Cretaceous ophiolites–ophiolitic mélanges in central Anatolia; Geological maps of ophiolites/listwaenites occurences in the Cürek–Divriği, Sivas (B), in the Güvenç–hekimhan, Malatya (C), in the Karakuz–Hekimhan, Malatya (D).

Table 1. A: Cobalt, Ni, As, Ag and Au concentrations (in ppm) of the listwaenites from Central Anatolia; 1B: Factor summary for listwaenite data sets of central Anatolia. Output from CORRESPONDENCE (Carr, 1995) for the data table 1 A.

A						**B**			
Sample No:	Co	Ni	As	Ag	Au	F1	F2	F3	F4
ADG-1	1	68	26	0.2	0.005	–0.3663	0.12577	–0.0204	–0.0155
ADG-2	80	1408	1700	30.4	0.023	–1.1104	–0.0232	–0.1957	0.00375
ADG-3	21	537	5.5	0.2	0.006	0.38464	0.05765	–0.0149	–0.0009
ADG-4	38	1066	3.1	0.2	0.013	0.40487	0.07429	–0.0119	–0.0013
ADG-5	23	1329	4.1	0.2	0.006	0.4044	0.16066	–0.017	0.00099
ADG-6	1	24	5.2	0.2	0.003	–0.0904	0.02598	–0.1829	–0.0287
ADG-6A	38	685	430	0.8	0.02	–0.6443	–0.0048	0.05722	–0.004
ADG-8	29	1552	16	0.2	0.003	0.38464	0.15316	–0.0142	0.00186
ADG-9	110	3327	1600	2.9	0.001	–0.4876	0.0634	0.04426	0.00196
ADG-10	20	419	34	0.2	0.025	0.20853	0.01829	–0.001	–0.0156
ADG-13	35	868	120	0.2	0.001	0.08056	0.04863	0.01439	0.00212
ADG-14	79	675	7.6	0.2	0.007	0.38406	–0.2726	0.01222	0.00034
ADG-15	31	234	200	9.8	0.003	–0.8402	–0.2291	–0.5723	0.01071
ADG-16	20	295	16	0.2	0.018	0.27462	–0.0669	–0.0059	–0.0158
ADG-17	5	9	1.6	0.2	0.001	0.08851	–1.3839	–0.2954	–0.0098
ADG-18	41	1136	29	0.2	0.014	0.34474	0.0711	–0.0066	–0.0014
ADG-19	180	3100	20	1.2	0.008	0.39504	–0.0274	–0.0097	0.00222
ADG-23	57	1350	7.4	0.2	0.01	0.39808	0.04413	–0.0078	0.00032
ADG-24	26	446	170	0.2	0.001	–0.3374	–0.0166	0.04732	0.00168
ADG-25	34	778	49	0.2	0.017	0.25146	0.03611	0.00089	–0.0042
ADG-26	81	1659	1500	2.5	0.005	–0.8992	0.01399	0.07291	0.00126
ADG-27	37	1258	870	0.4	0.01	–0.7252	0.0687	0.075	–5E–05
ADG-28	33	1108	2.9	0.2	0.026	0.40565	0.10158	–0.0138	–0.0052
ADG-29	39	519	4.6	0.2	0.005	0.38902	–0.1013	–0.0037	0.00012
ADG-34	84	1261	610	0.2	0.006	–0.4707	–0.0392	0.06609	0.00096
ADG-35	33	1674	500	0.2	0.011	–0.2285	0.11966	0.03636	0.00018
ADG-35A	4	130	26	0.6	0.004	–0.0561	0.07535	–0.0945	–0.0045
ADG-36	13	301	220	1.7	0.005	–0.7592	0.02311	–0.0181	–5E–05
ADG-37	3	33	5.7	0.2	0.004	0.01391	–0.1537	–0.118	–0.028
ADG-38	64	639	53	0.6	0.005	0.21242	–0.1927	0.002	0.00116
ADG-39	4	81	21	0.2	0.015	–0.1523	0.00843	–0.0216	–0.046
ADG-40	4	84	10	0.2	0.011	0.11889	0.01475	–0.0477	–0.0354
ADG-41	51	1481	9.5	0.5	0.02	0.39493	0.07933	–0.0163	–0.0017
ADG-42	76	223	140	2.2	0.007	–0.5005	–0.6962	–0.0458	0.00052
ADG-44	9	287	2.2	0.2	0.006	0.39049	0.9262	–0.0284	–0.0041
ADG-46	94	1730	1000	5.9	0.001	–0.5937	–0.0054	0.00738	0.00274
ADG-58	38	354	18	0.8	0.072	0.28327	–0.2292	–0.04	–0.0568
ADG-60	230	712	3.5	0.2	0.003	0.40151	–0.9647	0.06292	0.00398
ADK-22	26	416	69	0.2	0.001	0.0298	–0.0387	0.01814	0.00203
ADK-24	34	441	57	0.2	0.001	0.10876	–0.0971	0.01685	0.00226
ADK-25	34	686	190	0.2	0.001	–01786	0.01199	0.03611	0.0019
ADK-26	29	332	27	0.2	0.006	0.21467	–0.1427	0.00735	–0.0022
ADK-27	72	1130	47	0.2	0.001	0.30621	–0.0496	0.00542	0.00263
ADK-41	34	475	20	6	0.001	0.27457	–0.1079	–0.3542	0.00819
ADC-1	45	943	35	0.2	0.007	0.31583	0.01903	–0.0015	0.0004
ADC-2	33	1070	240	0.2	0.015	–0.0932	0.08262	0.02672	–0.0017
ADC-3	30	505	140	0.2	0.018	–0.1749	–0.0231	0.0357	–0.0069
ADC-4	63	1082	85	0.2	0.035	0.21708	–0.0248	0.01021	–0.0071
ADC-5	52	1510	37	0.2	0.006	0.34743	0.07876	–0.0059	0.00134
ADC-6	2	30	15	0.2	0.008	–0.4992	–0.0486	–0.069	–0.0548
ADC-7	39	1004	42	0.5	0.001	0.30238	0.05735	–0.012	0.0025
ADC-8	77	2052	28	0.2	0.016	0.37629	0.06536	–0.0061	0.00011

Table 1 continued

ADC-9	52	887	41	0.2	0.001		0.29419	–0.0278	0.0033	0.00251
ADC-10	55	1158	22	0.2	0.006		0.36237	0.02015	–0.004	0.00112
ADC-11	44	266	13	0.4	0.001		0.2955	–0.4429	–0.0009	0.00327
ADC-12	82	357	150	2.8	0.023		–0.3188	–0.5134	–0.0647	–0.0078
ADC-13	2	2	60	11	0.2		–0.0203	0.06821	–0.0653	–0.12
ADC-14	10	242	98	0.2	0.001		–0.381	0.03856	0.03803	0.0012
ADC-15	15	495	31	0.2	0.014		0.25002	0.09414	–0.0078	–0.0064
ADC-16	50	1127	17	0.2	0.006		0.37249	0.03417	–0.006	0.00104
ADC-17	77	1446	17	0.2	0.001		0.38163	–0.0054	–0.0026	0.00265
ADC-18	29	819	39	0.2	0.001		0.28816	0.07288	–0.0043	0.00225
ADC-19	150	3328	34	0.2	0.001		0.38571	0.03134	–0.0031	0.00266
ADC-20	41	1517	45	0.2	0.001		0.33349	0.11215	–0.0073	0.00234
ADC-21	63	2752	11	0.4	0.001		0.40193	0.13397	–0.0146	0.00246
ADC-22	38	572	20	0.4	0.009		0.32152	–0.0626	–0.0106	–0.0018
ADC-23	57	1004	29	0.2	0.01		0.33738	–0.0205	9.4E–05	–0.0003
ADC-24	30	2228	19	0.2	0.007		0.38951	0.17842	–0.0152	0.00138
ADC-25	40	1087	9.1	0.2	0.013		0.39012	0.06872	–0.0102	–0.0012
ADC-26	58	2288	13	0.2	0.008		0.39751	0.12233	0.0116	0.0014
ADC-27	30	1214	160	0.2	0.007		0.09021	0.11339	0.01068	0.00057
ADC-28	12	414	55	0.2	0.011		0.08839	0.0948	0.00302	–0.0055
ADC-29	9	194	29	0.2	0.003		0.05703	0.02249	–0.004	–0.0016
ADC-30	42	1502	1500	0.2	0.001		–0.9825	0.06457	0.09899	0.00111
ADC-31	35	222	18	0.2	0.006		0.22561	–0.4032	0.01841	–0.0037
ADC-32	53	1632	310	0.2	0.014		–0.027	0.07816	0.02361	–0.0002
ADC-33	4	29	72	0.2	0.013		–1.5307	–0.1047	0.09178	–0.041
ADC-34	62	1228	29	0.2	0.001		0.35058	0.00694	–0.0018	0.00256
ADC-35	79	1018	57	0.2	0.006		0.27282	–0.106	0.01162	0.00119
ADC-43	31	681	15	0.2	0.009		0.35407	0.02864	–0.0078	–0.0015
ADC-45	31	793	18	0.2	0.008		0.35209	0.05751	–0.0085	–0.0006
ADC-46	45	985	27	0.2	0.013		0.3404	0.02806	–0.0039	–0.0015
ADC-47	2	22	47	0.2	0.001		–1.4646	–0.052	0.05342	–0.0025
ADC-49	58	1124	490	0.2	0.007		–0.417	0.00624	0.05809	0.00053
ADC-53	3	20	2.3	0.2	0.005		0.1346	–0.3803	–0.213	–0.0607
ADC-54	10	49	6.4	0.2	0.012		0.12763	–0.5424	–0.0418	–0.0583
ADG-30	8	212	28	0.2	0.009		0.09143	0.05783	–0.0075	–0.0098
ADG-31	6	182	6.7	0.2	0.002		0.31297	0.08242	–0.0334	–0.0005
ADG-32	5	123	45	0.7	0.001		–0.3322	0.03305	–0.0801	–0.0059
ADG-67	49	1053	16	0.2	0.01		0.37224	0.02443	–0.0056	0.00251
ADK-35	4	80	120	2.3	0.037		–1.2666	–0.0129	–0.2418	–0.0555
ADK-36	5	96	88	1.8	0.001		–0.9206	–0.0145	–0.2104	0.00459
ADK-37	8	57	89	1.5	0.001		–1.2361	–0.166	–0.1823	0.0043
ADK-38	12	53	110	0.8	0.001		–1.3724	–0.2484	0.00298	0.0019
ADK-39	330	857	41	0.2	0.001		0.31749	–1.098	0.08068	0.00499
ADK-48	68	1136	15	0.2	0.001		0.37793	–0.0345	–0.0013	0.00267
						Co	0.20225	–0.893	0.02421	9.5E–05
						Ni	0.20395	0.04649	–0.0013	1.6E–05
						As	–1.1933	0.00327	0.01516	–2E–06
						Ag	–1.2376	–0.4494	–2.3126	0.00377
						Au	–0.0266	–0.2239	–0.3923	–2.4604

ADC = Cürek, ADG = Güvenç, ADK = Karakuz

Co (1ppm), As (0.5 ppm), and Au (2 ppb) are determined by INAA, Ni (1 ppm) and Ag (0.4 ppm) are determinde by ICP. Numbers with parenthesis are indicating detection limit of the analytical instruments.

5. Attribute Co shows big association with any sample in all the correspondence plots. The only exceptions (Figure 2) Co weakly associated with any sample in all the plots.

6. There is a strong correlation between Co and Ni-As in all the correspondence plots (Figure 2 through 7). There is no association among Co and Au.

7. Attributes Co, Ni, and As have a good association with most of the listwaenite individuals in all three sampling sites (Figures 3, 4, 5, 6, and 7).

8. Some Listwaenite samples are not associated among themselves, and are almost isolated from each other (Figure 2 through 7).

The negative association among Co-Au, and listwaenite samples-Co, Au may indicate that the hydrothermal solution did not carry those elements at the same time interval during the formation of listwaenites or Co and Au complex were not in equilibrium with each other in hydrothermal solutions during the transportation. However, Co, Ni and Au are closely associated with As in listwaenites and were probably

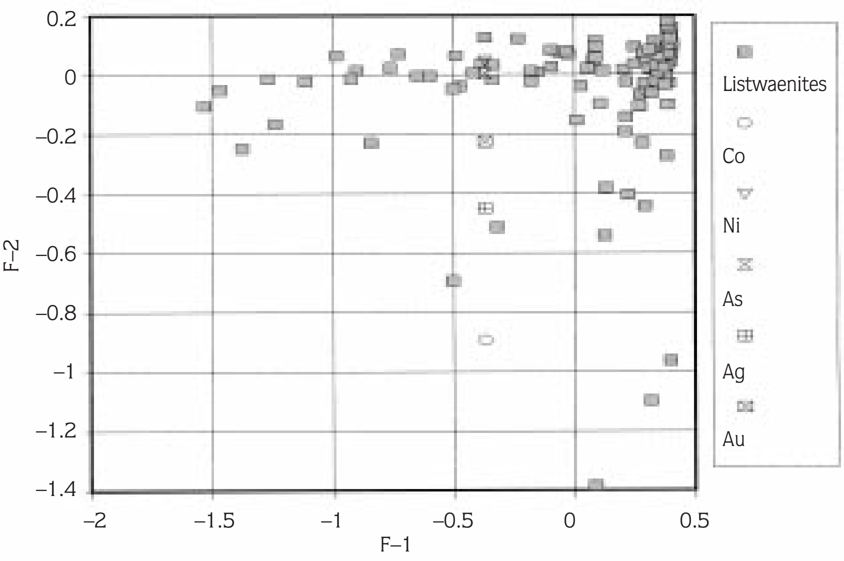

Figure 2. Correspondence analysis plot for the listwaenite data sets of central east Anatolia, Turkey. Factor 1 versus factor 2.

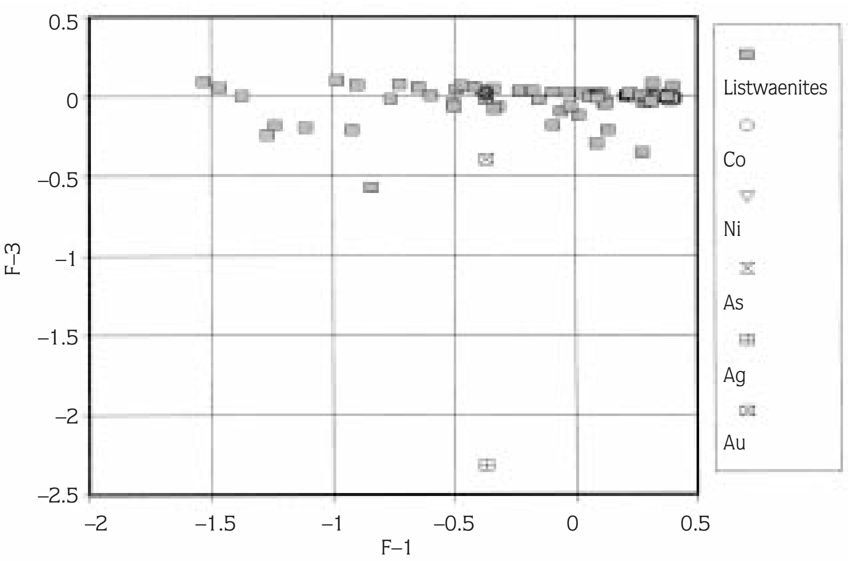

Figure 3. Correspondence analysis plot for the listwaenite data sets of central east Anatolia, Turkey. Factor 1 versus factor 3.

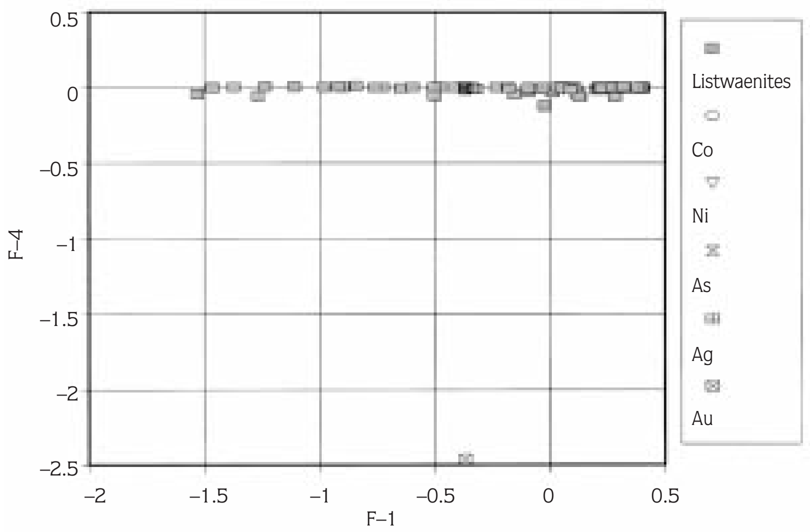

Figure 4. Correspondence analysis plot for the listwaenite data sets of central east Anatolia, Turkey. Factor 1 versus factor 4.

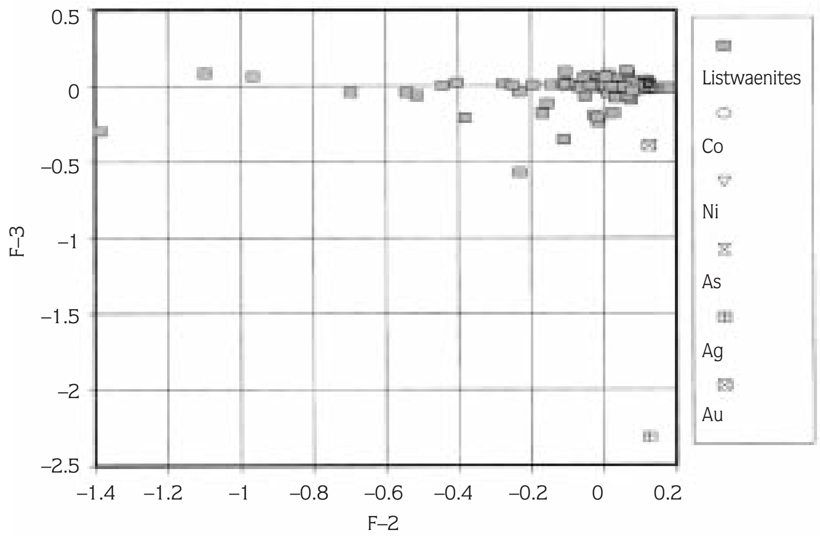

Figure 5. Correspondence analysis plot for the listwaenite data sets of central east Anatolia, Turkey. Factor 2 versus factor 3.

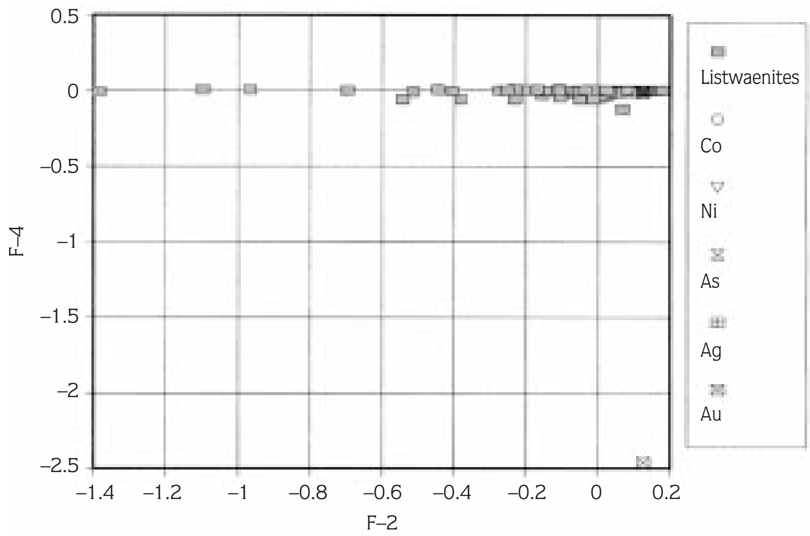

Figure 6. Correspondence analysis plot for the listwaenite data sets of central east Anatolia, Turkey. Factor 2 versus factor 4.

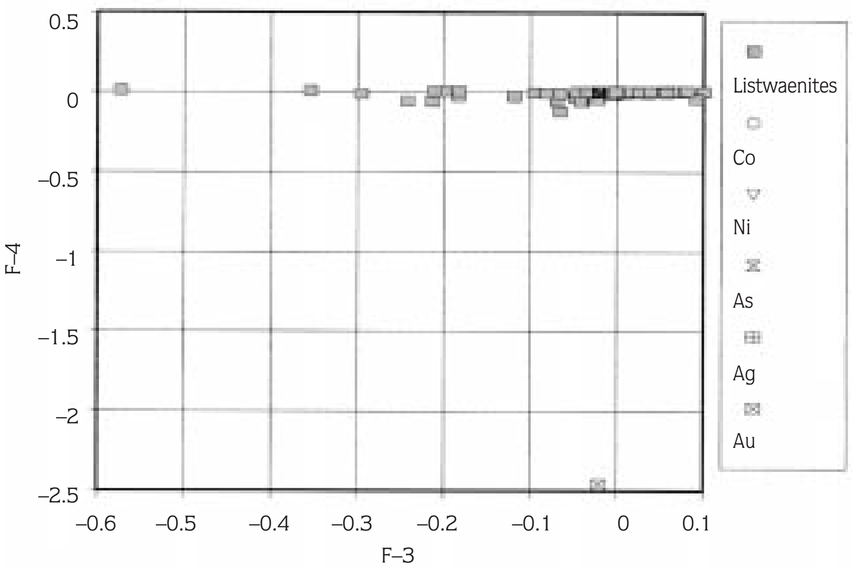

Figure 7. Correspondence analysis plot for the listwaenite data sets of central east Anatolia, Turkey. Factor 3 versus factor 4.

equilibrium in hydrothermal solution during the alteration of mafic-ultramafic rocks. Figures 2, 3, and 5 show that the Ag is not associated with As in listwaenites and this may suggest that Ag were introduced into the system by hydrothermal fluids in low concentrations. Most of the correspondence plots reveal the listwaenites in three different areas formed by the same hydrothermal-tectonic conditions with regarding to base and precious metal contents. Some of the listwaenite samples did not associate each other in all the correspondence plots probably due to following reasons: possible differences in composition, temperature and pH of hydrothermal solutions --silica-carbonate listwaenite bodies are characterized by low pH and low to moderate temperature (150-300 °C) however, carbonate listwaenite bodies were formed at high pH and moderate temperature (< 300 °C) (Uçurum, 1996); differences in the mineralogy of the host rocks; differences in tectonic regime, for example at Karakuz the listwaenite is in thrust contact with Quaternary sediments where as at Güvenç and Cürek listwaenites are in thrust of fault zone of late Cretaceous serpentinites.

Conclusions

The geological study by Uçurum (1996) indicate that the listwaenites were formed from serpentinite and serpentinized ultramafic rocks in the Divriği and Kuluncak ophiolitic mélanges by hydrothermal fluids in the late Cretaceous, and he concluded that concentration of base and precious metals in the listwaenites was probably determined by the presence and amount of Si in the hydrothermal fluids. Close association between Co-As, Ni-As and Au-As suggest that those elements were in equilibrium in the hydrothermal fluids.

The correspondence analysis–which is this study- and geological study by Uçurum (1996) confirm each other. Co-Ni-As and Au, has good correlation between each other however, correlation between Ag and other metals is not so good. In conclusion, Co, Ni and Au were introduced into hydrothermal fluids as arsenic complexes, and Ag was not in equilibrium with other metals in the hydrothermal fluids or it was introduced into the system in low concentrations.

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