# LISTWAENITES IN TURKEY: PERSPECTIVES ON FORMATION AND PRECIOUS METAL CONCENTRATION WITH REFERENCE TO OCCURRENCES IN EAST-CENTRAL ANATOLIA

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**Key words:** Listwaenites, Precious Metals, Central Anatolia, Hydrothermal Alteration, Turkey.

ABSTRACT

The low hydrothermal alteration of serpentinites from the ophiolite complexes in Turkey has formed listwaenites with either mineralized or non-mineralized and scattered through the three-ophiolite belts in Anatolia, Turkey. The listwaenite occurrences and associated mineralization in Turkey are reviewed, taking into account the location and description used in literature. The geology and geochemistry of the listwaenites in east central Anatolia serve as a reference to illustrate the characteristics of listwaenite formation and precious metal concentrations in ophiolite belts of Turkey.

The late Cretaceous (Pre-Maastrichtian) alteration of serpentinite bodies in the Divriği and Kuluncak ophiolitic mélanges, in east central Anatolia has formed two distinct types of listwaenite. The earliest is silica-carbonate listwaenite (type I), which is dominated by silica+calcite+dolomite+ankerite±magnesite. Later, carbonate listwaenite (type II) comprise calcite+dolomite+ankerite±magnesite, and lack any significant introduction of silica.

In the Divriği and Kuluncak ophiolitic mélanges the most of the silica-carbonate (type I) and carbonate (type II) listwaenite are formed along thrust fault zones. In clearly fault-related listwaenites, thrust fault(s) acted as pathway for hydrothermal fluids. In non fault-related listwaenites, hydrothermal fluids moved along highly serpentinized microfractured, stockworked and porous ultramafic rocks. The hydrothermal fluids involved in the formation of carbonate (type II) listwaenite differed from those that formed silica-carbonate (type I) listwaenite, which was enriched in $SiO_2$, as well as $CO_2$, Ca and $H_2O$, whereas those that formed carbonate listwaenite were $SiO_2$ deficient, and enriched only in $CO_2$, Ca and $H_2O$.

## PRESENT STATE OF KNOWLEDGE

The current state of knowledge of listwaenite is briefly reviewed so that the relevance of the research topic to the field area and the methods of study employed can be fully appreciated. The term listwaenite was first introduced to the literature of mineralogy by Rose (1837) from the Urals area, where he referred to silica-carbonate alteration rocks of ophiolite. Much more has been written on the topic by Russian field geologist and researchers (Bok, 1956; Ploshko, 1963; Kashkai and Allakhverdiev, 1965, 1971; Scherban, 1967; Scherban and Borovikova, 1970; Goncharenko, 1970; Sazanov, 1975; Abovian, 1978; Kuleshevich, 1984; Spridinov, 1991). These listwaenites include many types of silica and carbonate-bearing rocks, each with different phyllosilicate mineral associations; namely silica-carbonate rocks, serpentine silica-carbonate rocks, iron silica-carbonate rocks, chlorite silica-carbonate rocks, talc silica-carbonate rocks, and chromian mica silica-carbonate rocks.

The differences in genetic types of listwaenite, the differing petrochemical properties, and mineralogical composition have produced a need to systematize and make more precise the nomenclature of these interesting rocks. Kashkai and Allakhverdiev, (1965) classified listwaenites based on four main headings as follows; 1-) By genesis: pneumatogenic-metasomatic, hydrothermal-metasomatic, and bimetasomatic listwaenites. 2-) By original rocks: ortholistwaenites, formed by metasomatic alteration of ultramafic rocks or other mafic igneous rocks; paralistwaenite from sedimentary rocks; epilistwaenite from metamorphic rocks. 3-) By mineral composition. Depending on the content of the main components the nomenclature of genetic types is established, for instance: quartz-carbonate, carbonate-quartz, talc, chlorite listwaenite. 4-) By metalliferousness. On the basis of content of ore and ore-silicate minerals a nomenclature is given, for instance, gold-bearing, nickelifereous, listwaenites etc.

Listwaenite is typically composed of quartz, carbonate minerals (magnesite, ankerite, and dolomite), and/or fuchsite or mariposite, together with sulfides and a number of other accessory minerals. With a few exceptions, listwaenites are formed through the metasomatic/hydrothermal alteration of serpentine (Kashkai and Allakverdiev, 1965; Capedri and Rossi, 1973; Buisson and Leblanc, 1986). They are evolved as products of two successive stages of same process: the serpentinization of ultrabasites followed by metasomatic alteration (Kashkai and Allakhverdiev, 1965). Listwaenitization of serpentinites occurs immediately after the autometamorphism of the derivatives of ultrabasic magma. Listwaenites occur as lenses, pods, and vein like bodies within ultrabasic units of Alpine-type ophiolite-ophiolitic melanges. Fluid movement along fractures produces dike-like listwaenites, the length of which can range in hundreds and the thickness in tens of meters.

Silica, CaO, MgO and $Fe_2O_3$ are common major oxides in the listwaenites. Minor elements commonly enriched to levels greater than in the serpentinites include Co, Cr, Ni, As, Cu. Antimony, Hg, Au and Ag are rarely enriched to ore grade.

Listwaenite research is of practical as well as theoretical importance because listwaenites host or are spatially associated worldwide with gold, arsenic, cobalt, nickel, tungsten and mercury deposits (Zhelobov, 1979; Kashkai and Allakhverdiev, 1965; Gorchakov and Lishnevsky, 1982; Goncharenko, 1984; 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).

A listwaenite and cobalt association is reported in Morocco (Leblanc, 1986, 1988, 1991; Leblanc and Billaud, 1982; Leblanc and Fischer, 1990), where cobalt has been mined at the Bou Azzer deposit. Listwaenitization is well known in the California Coast Ranges where it is associated with mercury mineralization at the Knoxville, Horison, Reed, Red Elephant, New Almaden, Sulphur Bank and New Idria mines (Barnes et. al., 1973; Henderson, 1969; Shields, 1983; Studemeister, 1984; Sherlock and Logan, 1995). Au and Ag associations with listwaenites have been reported all over the world. For example in the Caucasus (Kurdyukow et al., 1977; Kashkai and Allakverdiev, 1965; Plashko, 1963), in the North American Cordillera (Dussell 1986; Graham, 1988; Ash and Arksey, 1990; Landefield, 1988; Landefield and Silberman, 1987; Knopf, 1929), in the Appalachian and Ontario areas (Auclair et al., 1993; Moritz et al., 1990; Moritz and Crocket, 1990, 1991; Moritz, 1988; Dupuy et al., 1981), and in Archean dunites in Yilgarn block, Australia (Martyn and Johnson, 1986; Donaldson, 1981). Various base and precious metal listwaenite association is also reported in the ultramafic-mafic belts of the Arabian shield, Saudi Arabia (Buisson and Leblanc, 1986), in central Euboea, Greece (Capedri and Rossi, 1973; Capedri, 1974), in the Barberton greenstone belt, South Africa (De Ronde et al., 1991), in Ligurian ophiolites, Italy (Pipino, 1980); in the Shusha and Lachin regions, Azerbaijan, and in Bessaza, northern Balkhash and western Kalba regions, Kazakhstan (Kashkai and Allakhverdiev, 1965). Listwaenite association with various base and precious metal occurrences in Kyrgyzstan, Armenia, Tuva Ultramafic complex, western Transbaikalia and the Sayans are briefly reported by Kashkai and Allakhverdiev (1965).

## LISTWAENITE RESEARCH IN TURKEY

The low hydrothermal alteration of serpentinites from the ophiolite complexes in Turkey has formed listwaenites either mineralized or non-mineralized and scattered through the three-ophiolite belts in Anatolia (Fig. 1 and Table 1). The earliest research on listwaenites and associated mineralization in Turkey is described by Legros (1969) near the iron mines at Divriği in Sivas province. Leo et al., (1978) conducted research on Kuluncak ophiolite in Kuluncak-Malatya and concluded that the large part of a serpentinite-gabbro complex is covered by a silica-carbonate cap with disseminated or massive magnetite and vein of dolomite and quartz. Aydal (1987) conducted the first complete study of a listwaenite occurrence near the village of Gemiköy in Kastamonu province in north Anatolia and discussed its mineralogy, chemistry and gold enrichment. He concluded that the Gemiköy listwaenite is autometamorphic in genesis. Tüysüz (1991), Tüysüz and Erler (1993) reported on listwaenite near Çermelikoy-Komik in the Kağızman region of Kars province, and defined two phases of listwaenite in a late Cretaceous ophiolite. They suggested that this listwaenite occurrence is subduction-related in origin and that listwaenites served as source rocks for placer gold in the region. Yılmaz et. al., (1991) described listwaenite in the ophiolite sequence near Güvenç in the Hekimhan region in Malatya province. Genç et al., (1990) and Genç (1992) recently reported on mercury-arsenic ore hosted by silica-carbonate alteration in a early Cretaceous ophiolite at Narman, Erzurum province. They concluded that the mercury ore in the listwaenite was formed by hydrothermal solutions. Fluid inclusion and temperature calculations from $d^{18}O$ contents of carbonates indicate a formation temperature between $56^0C$ and $163^0C$. The $d^{13}C$ contents of the carbonates from listwaenites indicate that the C is sedimentary in origin. Larson and Erler (1992) reported that mercury and antimony deposits in Karakaya, Sivrihisar-Eskişehir, are in a silica-carbonate alteration zone. Larson and Erler (1992) and Erler and Larson (1992) concluded that listwaenite occurrences in Kaymaz near Sivrihisar-Eskişehir and in İnegöl-Bursa show enrichment in precious metal concentration, and that those at Kaymaz are at least locally of ore grade (>3 g Au/t). Boztuğ et al., (1994) described listwaenite occurrences near Alacahan (Sivas) and concluded that the listwaenites in the area are enriched in As, Ni, Co, Cd, Pb and Zn. Listwaenite occurrences in the Karakuz area were first reported by Uçurum et al., (1994) who also concluded that listwaenites in the Divriği and Hekimhan areas have very low precious metal concentrations. Later Uçurum (1996,1998), Uçurum and Larson (1995; 1999) determined that the listwaenites in the Divriği and Hekimhan areas are enriched in Co, Ni, Cr, and As, although Au and platinum group elements are in very low concentrations. Listwaenites in Karacakaya, Yunusemre-Eskişehir, was studied by Koç and Kadıoğlu (1996) and they concluded that the listwaenites contain silver ranging from 0.0004 g/t to 10.2 g/t. Reçber et al., (1997) also reported that the Yunusemre listwaenites in Eskişehir contain silver up to 4.7 g/t. Çiftçi (1998) reported that the listwaenite occurrence in İmranlı-Sivas and Refahiye-Erzincan contain Ni-Sulfide mineralization. Oygür and Erler (1999) reported another Hg-Sb associated listwaenite occurrence in Körkuyu, Şaphane-Kütahya.

## EAST CENTRAL ANATOLIAN LISTWAENITES

### General geological setting

The study of listwaenite outcrops has been completed in three distinctive areas in the Tauride tectonic belt of central Anatolia, Turkey (Fig. 1A). The three areas that were studied occur in two different ophiolitic mélanges within the Tauride ophiolite belt (Fig. 1B). These are the Divriği ophiolitic mélange (Tunç et al. 1991) in Sivas, and the Kuluncak ophiolitic mélange (Yılmaz et al. 1991) in Hekimhan-Malatya (Fig. 1C). Both mélanges developed during the late Cretaceous (Tunç et al. 1991; Yılmaz et al. 1991).

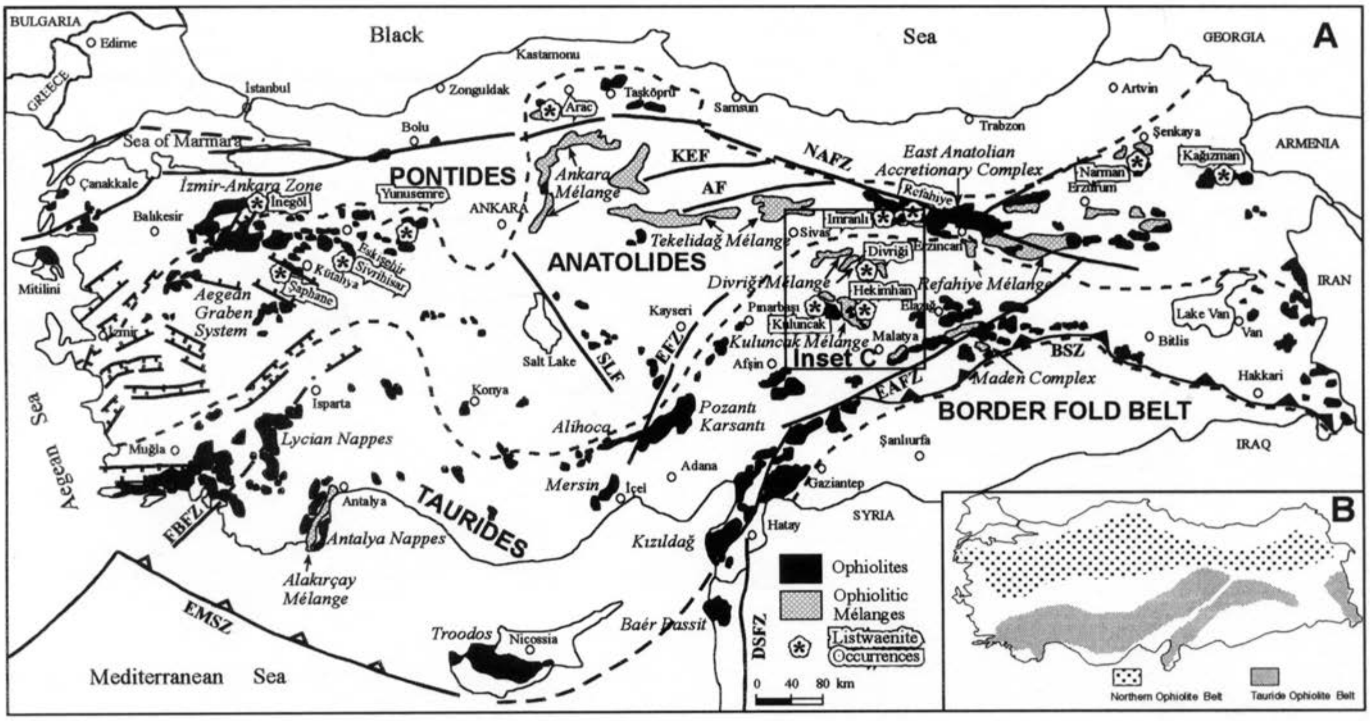
The rock units in the Divriği ophiolitic mélange (Fig. 2) include the Upper Jurassic-Lower Cretaceous Akdağ limestone, the Upper Cretaceous Çaltı ultramafic rocks, and the Cürek listwaenite. The Divriği ophiolitic mélange is intruded by the Lower Cretaceous Murmano pluton. The above tectono-stratigraphic sequences is continued by the Eocene-Paleocene Ekinbaşı metasomatite and the Quaternary Kilise Formation.

The oldest sequence of rocks in the Kuluncak ophiolitic mélange in the Güvenç area (Fig. 3) is the Karadere ultramafics, which are 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 dike in the late Cretaceous. 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 (Fig. 4) is similar to that in Güvenç, but, gabbro, radiolarite and Miocene volcanic rocks are not present. The Miocene is represented by the Ciritbelen Formation in Karakuz, and the Karakuz iron deposit is hosted by a late Cretaceous sub-volcanic trachyte dike.

## Geology of the listwaenites

Listwaenitic alteration of serpentinite is recognized to form two different rock types which differ from one another in their mineralogy, chemical composition, stratigraphic position, and the timing of their formation (Uçurum, 1996). Listwaenites are present as both silica-carbonate (type I) listwaenite and carbonate (type II) listwaenites in the



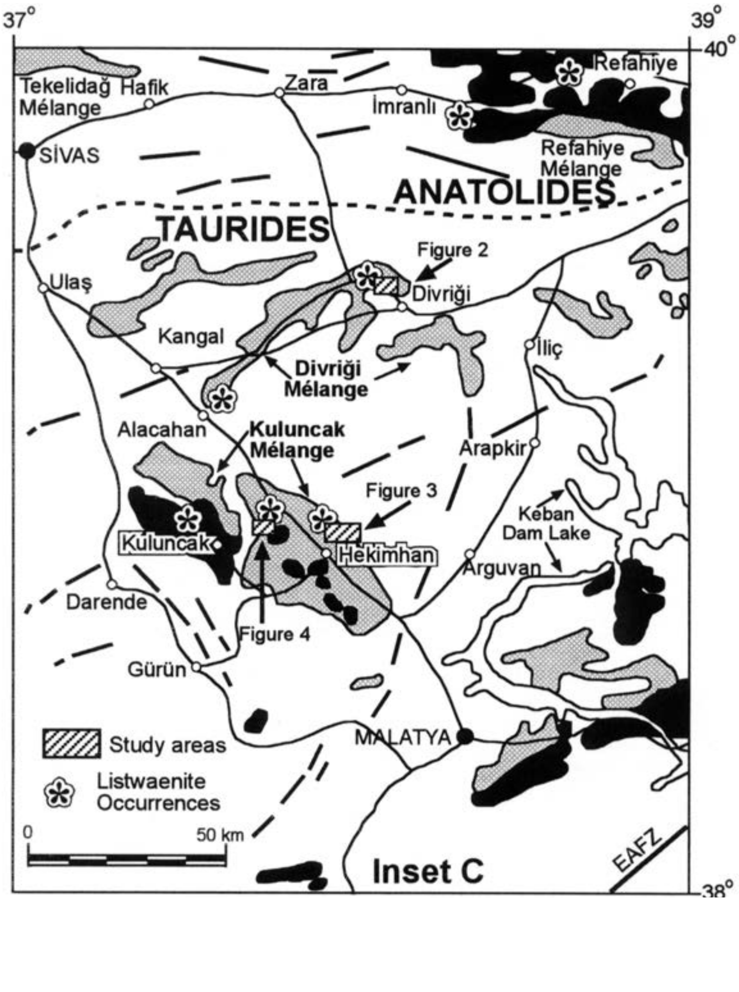




Fig. 1 - A-) Distribution of the Mesozoic ophiolites-ophiolitic mélanges and the listwaeinite occurrences in Turkey and the eastern Mediterranean. KEF: Kırıkkale-Erbağa Fault, AF: Almus Fault, EMSZ: East Mediterranean Subduction Zone, DSFZ: Dead Sea Fault Zone, NAFZ: North Anatolian Fault Zone, EAFZ: East Anatolian Fault Zone, BSZ: Bitlis Suture Zone, SLF: Salt Lake Fault, EFZ: Ecemiş Fault Zone, BFFZ: Burdur-Fethiye Fault Zone (Data for ophiolite-ophiolitic mélanges after İzdar and Ünlü, 1977; Juteau, 1980; Gass, 1980; Yılmaz, 1981; Ketin, 1983; Yazgan, 1983; Robertson and Dixon, 1984; Yılmaz and Maxwell, 1984; Delaune-Mayere, 1984; Tankut, 1984; Yılmaz, 1985; Bingöl, 1989; Dilek and Moores, 1990; Tunç et al., 1991; Yılmaz et al., 1991; Barka et al., 1995; Dilek et al., 1999). Tectonic boundaries (dashed lines) are derived from Ketin (1966). Data for listwaenite locations are from Table 1; B-) Ophiolite belts of Turkey after Juteau (1980); C-) Location map of the study areas and the distribution of the late Cretaceous ophiolites-ophiolitic mélanges in east central Anatolia, Turkey.

Table 1 - Listwaenites and associated mineralization in Turkey

| Locations of listwaenite occurrences | Associated Mineralizations | Source of References |
|---|---|---|
| Sivas-Divri_i | Fe | Legros (1969) |
| Malatya-Kuluncak | Fe | Leo et al (1978)<br>Yıldızeli et al., (1987) |
| Sivas-Alacahan | Fe± Au | Yıldızeli et al., (1987)<br>Gültekin (1993)<br>Boztu_ et al., (1994) |
| Kastamonu-Araç-Gemiköy | ± Au | Aydal (1989) |
| Erzurum-Narman* | Hg-Sb | Genç et al (1990)<br>Genç (1992) |
| Kars-Ka_ızman-Çermeli, Komik | ± Au | Tüysüz (1991)<br>Tüysüz and Erler (1993) |
| Bursa-_negöl-Sülüklüköy | Au-Ag | Larson and Erler (1992)<br>Erler and Larson (1992) |
| Eski_ehir-Sivrihisar-karakaya | Hg-Sb | Larson and Erler (1992)<br>Erler and Larson (1992) |
| Eski_ehir-Sivrihisar-kaymaz* | Au-Ag | Larson and Erler (1992)<br>Erler and Larson (1992) |
| Sivas-Çetinkaya | -------- | Gültekin (1993) |
| Eski_ehir-Yunusemre-Karacakaya | Ag±Au | Koç and Kadıoğlu (1996) |
| Malatya-Hekimhan-Güvenç | Co, Ni, As, ±Au, ±Ag | Uçurum (1996, 1998)<br>Uçurum et al (1994, 1997)<br>Uçurum and Larson (1995, 1999) |
| Malatya-Hekimhan-Karakuz | Co, Ni, As, ±Au, ±Ag | Uçurum (1996, 1998)<br>Uçurum et al, (1994, 1997)<br>Uçurum and Larson (1995, 1999) |
| Sivas-Divri_i-Cürek | Co, Ni, As, ±Au, ±Ag | Uçurum (1996, 1998)<br>Uçurum et al (1994, 1997)<br>Uçurum and Larson, (1995, 1999) |
| Eski_ehir-Yunusemre | Ag±Au | Reçber et al (1997) |
| Sivas-_mranlı | Ni-Sulfide, ±Ag±Au | Çiftçi (1998) |
| Refahiye-Erzincan | Ni-Sulfide, ±Ag±Au | Çiftçi (1998) |
| Erzurum-Pasinler-Tanktepe | Au±Ag | M. Yılmaz(TÜPRAG) (1999)<br>Personal communication |
| Kütahya-_aphane-Körkuyu | Hg-Sb | Oygür and Erler (1999) |

* It is ready to operate or pending for operation.

Güvenç (Fig. 3) and Karakuz (Fig. 4) areas in the Kuluncak ophiolitic mélange, whereas in the Cürek area (Fig. 2) of the Divriği ophiolitic mélange only silica-carbonate listwaenite is present. Most silica-carbonate listwaenite occurs along thrust faults which border the ophiolitic block within the ophiolitic mélange. Carbonate listwaenite is formed by non-fault related processes in Güvenç, whereas in Karakuz both silica-carbonate and carbonate listwaenite form along thrust faults.

The clear stratigraphic relationship between silica-carbonate and carbonate listwaenite in the Güvenç area suggests that the silica-carbonate (type I) listwaenite bodies are older and are followed by later carbonate (type II) listwaenite formation in the Divriği-Hekimhan region.

***Type I.*** Silica-carbonate listwaenites are present in all of the study areas (Figs. 2, 3, 4) and are either formed along and adjacent to thrust faults or within highly serpentinized porous and fractured ultramafic rocks.

Silica-carbonate (type I) listwaenite bodies in the Cürek area grade vertically into serpentinite from which they were derived. They range in thickness from 2-3 m to a maximum of 100 m. At the serpentinite-listwaenite contact there is a transitional zone which contains angular serpentinite blocks, (2-3 cm in diameter), chromite relics, and silica-carbonate minerals. The thickness of the transitional zone ranges from 5 cm to 60 cm. A silicic zone overlies the transitional zone and is composed of quartz, dolomite, calcite, and ankerite with hematite, magnetite and chromite. Listwaenite at Güvenç is exposed between Eskikent village and Güvenç village as silica-carbonate (type I) and its (Fig. 3) north and south boundaries are controlled by thrust faults. Both silica-carbonate (type I) and carbonate (type II) listwaenites in the Karakuz area are formed along thrust fault zones in serpentinite (Fig. 4).

In the Kızılcakale outcrop in the Karakuz area (Fig. 5) and southwest of Çulhalı village in the Güvenç area (Fig. 3), a sub volcanic trachyte intrudes the listwaenites. Leo et al. (1978) determined the age of a trachyte dike in the Kuluncak area some 10 km west of Karakuz area to be 71.1±1.6 to 74.3±1.7 Ma or equivalent to Maastrichtian. Late Cretaceous (Pre-Maastrichtian) is the accepted formation age for listwaenite in both the Güvenç and the Karakuz areas due to contact relationship between listwaenites and trachytes. There is not any contact relation between Murmano pluton and listwaenites in Cürek area. The age of the Murmano pluton is considered to be late Cretaceous by Sezer (1972), and by Koşal (1973); early Cretaceous (Albian) by Zeck and Ünlü (1988), and late Cretaceous-Paleocene by Tunç et al. (1991). The Cürek listwaenite, therefore, formed before 74 Ma (Maastrichtian) and after the Murmano pluton.

***Type II.*** The carbonate (type II) listwaenites present in both the Güvenç (Fig. 3) and Karakuz (Fig. 4) areas and mostly formed in highly serpentinized porous and fractured ultramafic rocks in Güvenç with rare thrust fault-related occurrences and in the Karakuz area along and adjacent to a thrust fault. Carbonate listwaenite is present only in the Güvenç (Fig. 3) and Karakuz areas (Fig. 4). The outcrops appear as a listwaenite cap on serpentinized ultramafic rocks. The boundaries of the carbonate listwaenites in the Karakuz area (Fig. 4) are thrust faults as are the boundaries for silica-carbonate listwaenite.

## Geochemistry of the listwaenites

$SiO_2$, CaO, MgO and $Fe_2O_3$ are common major oxides in both listwaenite types. Other oxides such as $Ti_2O$, $Al_2O_3$, MnO, $K_2O$, $Na_2O$ and $P_2O_5$ are present in very low (less than 1%) concentrations (Table 2). Fig. 5, a $Fe_2O_3$-$SiO_2$-CaO+MgO ternary diagram shows that silica-carbonate listwaenites plot along and near the $SiO_2$-CaO+MgO pseudo-binary at values of > 40% $SiO_2$ and < 60% CaO+MgO, while carbonate listwaenites, plot very near the CaO+MgO corner. Some extreme high values of silica, such as 80% and 96% in silica-carbonate and 40% and 57% in carbonate were provided by samples from intensely quartz veined listwaenite outcrops, and the high value probably represents introduced silica by hydrothermal $SiO_2$ veining. The relatively low silica in two samples is due to calcite-dolomite veins in silica-carbonate listwaenite outcrops.

Differences in the amounts of $Fe_2O_3$, $SiO_2$, CaO+MgO in silica-carbonate (type I) and carbonate (type II) listwaenites suggest differences in alteration intensity or composition of ultramafic/mafic protolith and/or chemistry of hydrothermal fluids involved in the formation of silica-carbonate and carbonate listwaenites. During the silica-carbonate formation period the hydrothermal fluid is enriched in silica, whereas carbonate fluids were characterized by high concentrations

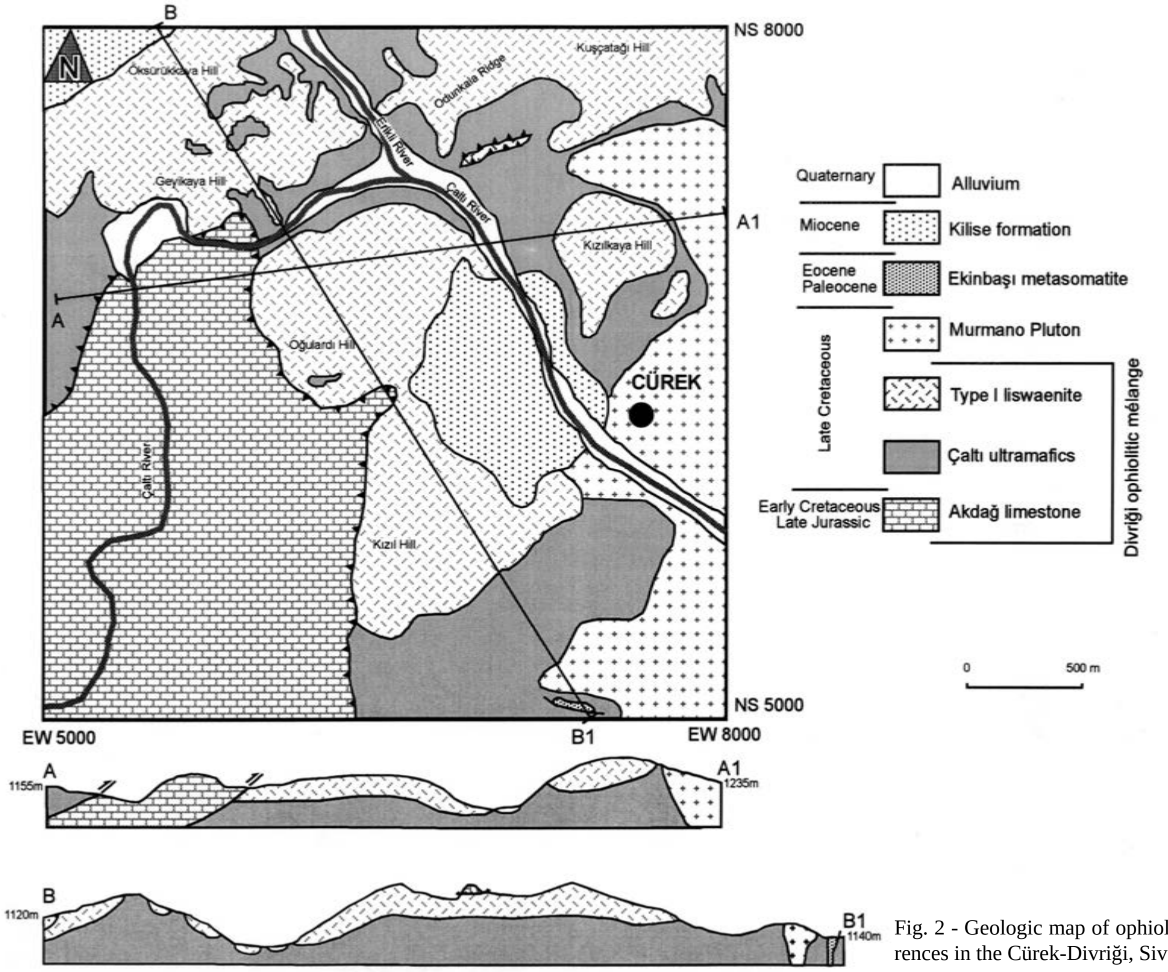



Fig. 2 - Geologic map of ophiolite/listwaenite occurrences in the Cürek-Divriği, Sivas (Uçurum, 1996).

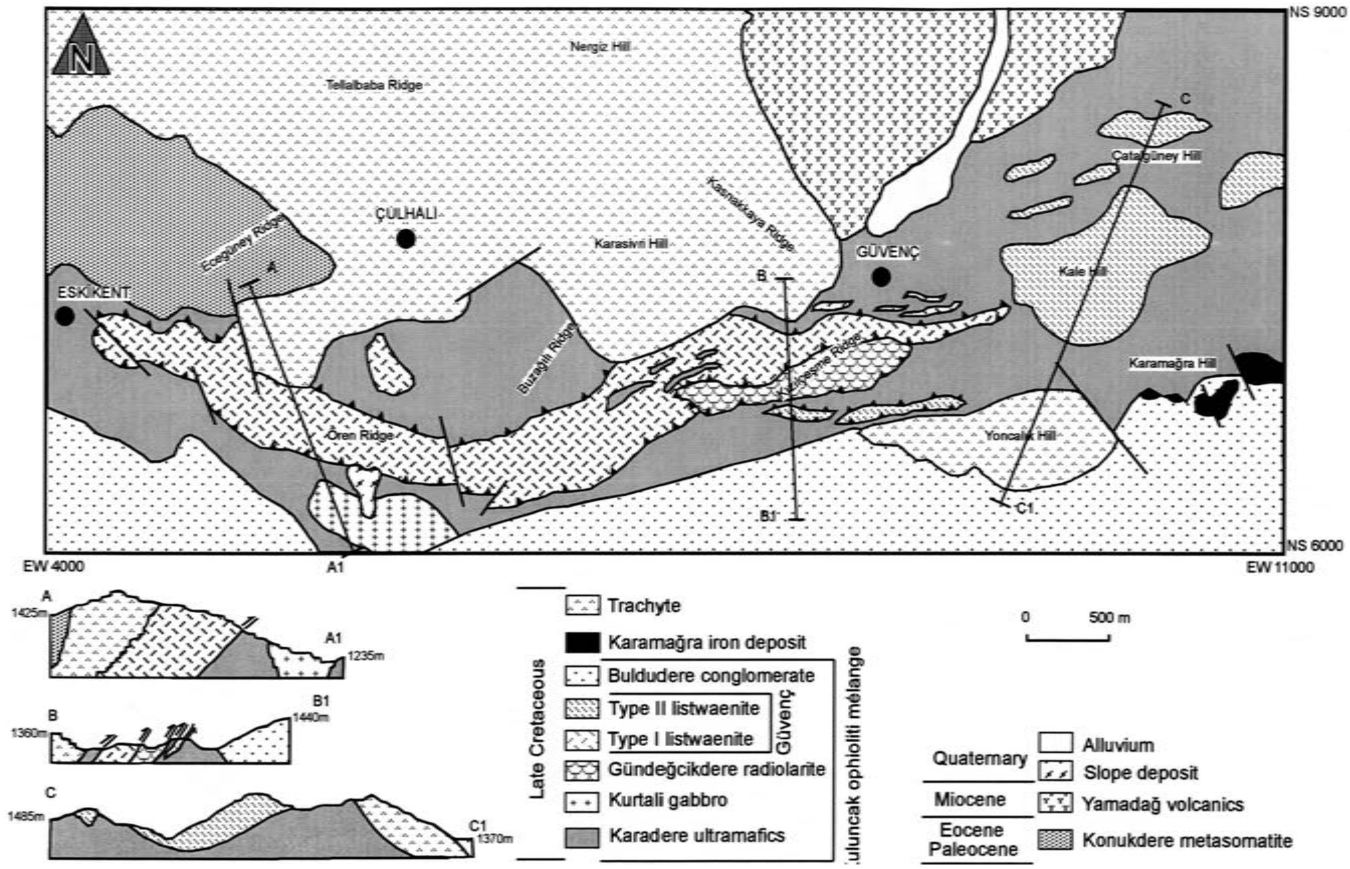



Fig. 3 - Geologic map of ophiolite/listwaenite occurrences in the Güvenç-Hekimhan, Malatya (Uçurum, 1996).

Table 2 - Major oxide concentrations of the listwaenites and associated alteration products of ultramafic rocks in the Divriği-Hekimhan region

| | Sample #s | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | LOI | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Type I----------- listwaenite** | ADG-10 | 30.53 | 0.01 | 0.36 | 4.8 | 0.17 | 12.66 | 19.18 | 0.08 | 0.01 | 0.01 | 31.25 | 99.06 |
| | ADG-23 | 29.66 | 0.01 | 0.42 | 7.23 | 0.13 | 25.9 | 3.47 | 0.08 | 0.01 | 0.01 | 32.51 | 99.42 |
| | ADG-26 | 37.19 | 0.03 | 0.33 | 10.28 | 0.59 | 11.76 | 12.5 | 0.09 | 0.01 | 0.01 | 25.7 | 98.5 |
| | ADG-37 | 79.99 | 0.01 | 0.28 | 1.5 | 0.1 | 2.87 | 6 | 0.04 | 0.09 | 0.03 | 8.46 | 99.36 |
| | ADG-42 | 96.16 | 0.01 | 0.87 | 1.92 | 0.01 | 0.16 | 0.06 | 0.09 | 0.1 | 0.02 | 0.81 | 100.21 |
| | ADK-25 | 30.02 | 0.01 | 0.32 | 5.69 | 0.19 | 13.39 | 19.2 | 0.23 | 0.01 | 0.01 | 30.4 | 99.46 |
| | ADK-26 | 56.09 | 0.02 | 0.49 | 2.84 | 0.14 | 9.14 | 12.25 | 0.11 | 0.01 | 0.01 | 18.54 | 99.63 |
| | ADK-27 | 28.16 | 0.03 | 0.24 | 5.36 | 0.39 | 12.86 | 20.49 | 0.08 | 0.03 | 0.03 | 31.15 | 98.83 |
| | ADK-41 | 52.9 | 0.01 | 0.27 | 5.99 | 0.23 | 8.09 | 12.84 | 0.03 | 0.02 | 0.02 | 18.82 | 99.19 |
| | ADC-13 | 96.58 | 0.01 | 0.54 | 0.79 | 0.02 | 0.39 | 0.22 | 0.13 | 0.05 | 0.01 | 1.02 | 99.76 |
| | ADC-21 | 17.83 | 0.01 | 0.64 | 3.34 | 0.08 | 15.66 | 24.03 | 0.1 | 0.01 | 0.01 | 37.36 | 99.06 |
| | ADC-29 | 94.53 | 0.02 | 0.74 | 1.72 | 0.02 | 0.23 | 0.18 | 0.18 | 0.01 | 0.01 | 1.27 | 98.9 |
| | ADC-45 | 49.9 | 0.02 | 0.3 | 3.46 | 0.11 | 9.32 | 14.22 | 0.12 | 0.02 | 0.01 | 22.16 | 99.63 |
| | ADC-57 | 7.7 | 0.02 | 1.42 | 7.8 | 0.11 | 38.47 | 0.32 | 0.01 | 0.01 | 0.02 | 13.88 | 100.01 |
| | **Average** | **50.52** | **0.02** | **0.52** | **4.48** | **0.16** | **11.49** | **10.35** | **0.10** | **0.03** | **0.02** | **19.52** | **99.36** |
| **Type II---------- listwaenite** | ADG-31 | 3.04 | 0.01 | 0.17 | 7.12 | 0.73 | 16.32 | 27.86 | 0.03 | 0.02 | 0.01 | 43.37 | 98.65 |
| | ADG-32 | 5 | 0.01 | 0.05 | 6.6 | 0.91 | 16.05 | 27.09 | 0.02 | 0.01 | 0.01 | 42.31 | 98.05 |
| | ADG-67 | 41.63 | 0.01 | 0.12 | 2.87 | 0.05 | 23.44 | 1.94 | 0.03 | 0.02 | 0.01 | 27.94 | 98.03 |
| | ADK-35 | 0.98 | 0.01 | 0.16 | 5.9 | 0.63 | 16.94 | 29.41 | 0.04 | 0.05 | 0.01 | 44.36 | 98.47 |
| | ADK-37 | 1.16 | 0.01 | 0.44 | 4.72 | 0.44 | 17.81 | 28.92 | 0.03 | 0.11 | 0.01 | 44.75 | 98.41 |
| | ADK-39 | 57.13 | 0.01 | 0.22 | 5.33 | 0.19 | 7.8 | 10.9 | 0.02 | 0.01 | 0.01 | 16.76 | 98.36 |
| | ADK-48 | 4.52 | 0.01 | 0.27 | 3.94 | 0.11 | 19.43 | 26.58 | 0.02 | 0.01 | 0.01 | 42.81 | 97.69 |
| | **Average** | **16.21** | **0.01** | **0.20** | **5.21** | **0.44** | **16.83** | **21.81** | **0.03** | **0.03** | **0.01** | **37.47** | **98.24** |

ADG = Güvenç; ADK= Karakuz; ADC = Cürek. Oxides are from XRF-Fusion disks, LOI at 1000 °C.

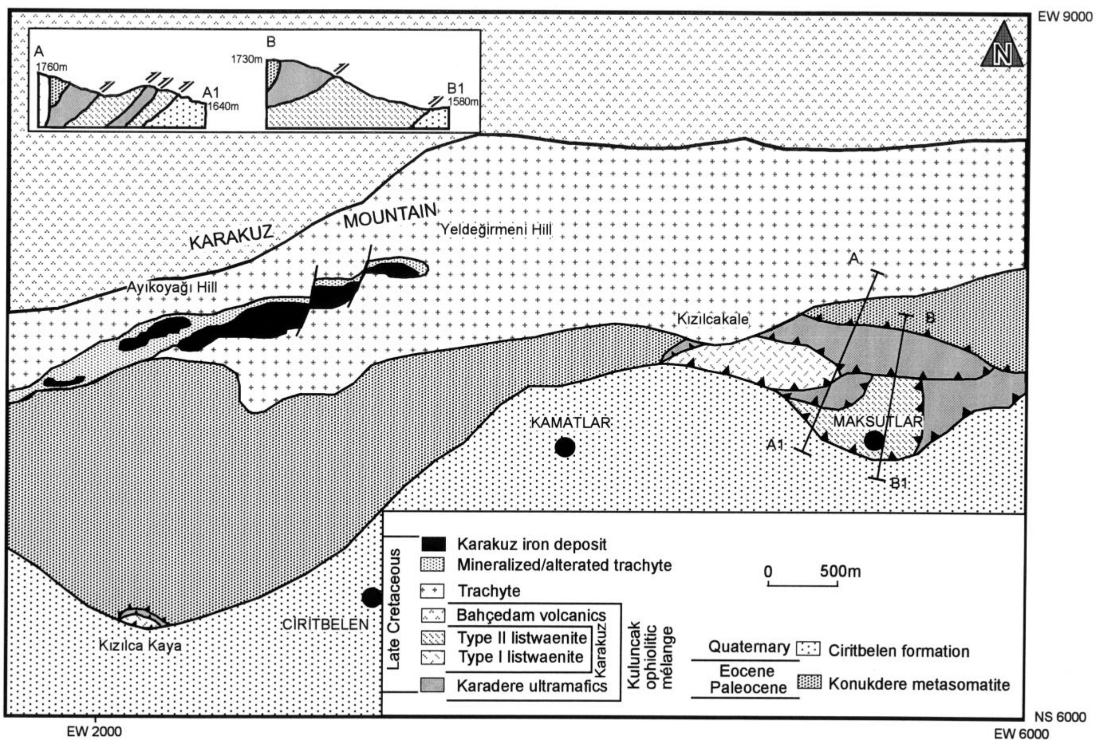



Fig. 4 - Geologic map of ophiolite/listwaenite occurrences in the Karakuz-Hekimhan, Malatya (Uçurum, 1996).

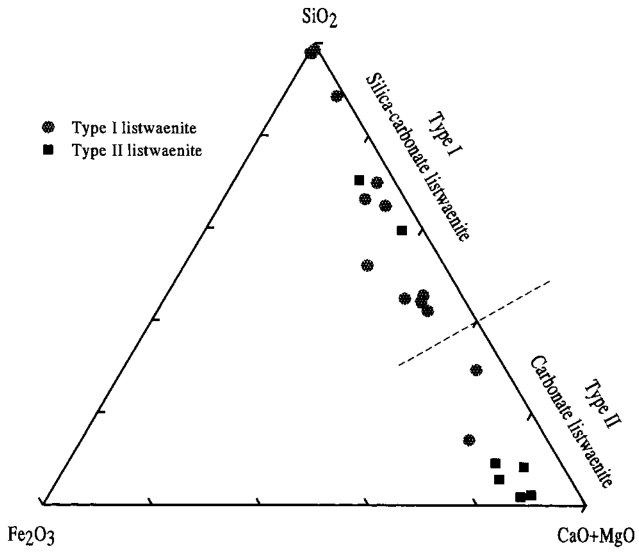



Fig. 5 - Plotting of listwaenites in $SiO_2$-$Fe_2O_3$-CaO+MgO ternary diagram. Dashed line divides the silica-carbonate (type I) and carbonate (type II) listwaenites. Data are from Table 2.

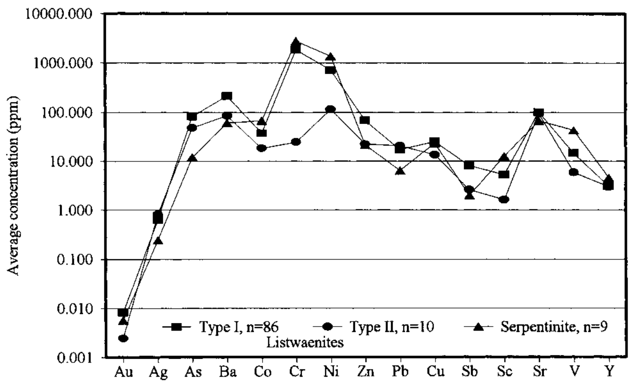



Fig. 6 - Multiple element spider diagram of listwaenites and serpentinites from Divriği and Hekimhan regions. Data are from Table 3.

of Ca and Mg. In addition, weathering possibly affected the chemistry of listwaenites as well as chemically different hydrothermal fluids. Weathering is a possibility tes are basically derived. Serpentinites in the Divriği-Hekimhan district with 35-41 % $SiO_2$ (Uçurum, 1996) compare well with other serpentinites in the world ( e.g. Deer et al. 1962; Hess et al. 1952; Brindley and Zusmman, 1957; Wicks and Plant, 1979). A second possibility is that the silica from serpentinites dissolved into the hydrothermal fluid during the formation of carbonate listwaenite and were taken out from the environment by the remaining fluid, which was enriched in silica in a high pH and low temperature environment. For carbonate listwaenite bodies this makes sense because silica is more soluble at high pH (≥ 9) than at lower pH, while the solubility of Ca increases with decreasing temperature (as much as 25-60 $^0$C) at low partial pressures of $CO_2$ ($3x10^{-4}$ atm) (Faure, 1991). This suggests that the hydrothermal solution for carbonate listwaenite was characterized by moderate-high temperature and high pH.

Chemical analyses of base and precious metals of listwaenite and associated rock units indicate that the As, Ba, Zn, Pb, Cu and Sb are enriched in listwaenite with respect to associated serpentinite and very locally Au, Ag and Zn are also highly enriched (Table 3, Fig. 6). This suggests that hydrothermal fluids introduced those elements during the formation of the listwaenites. Presence and amount of silica were probably the main controls that defined the concentrations of those elements in hydrothermal fluid, because silica-carbonate listwaenite is more enriched in As, Ba, Cr, Ni and Sb than is carbonate listwaenite. Serpentinite is characterized by high Co, Cr and Ni concentrations in the Divriği and Hekimhan regions (Fig. 6). However, a number of listwaenite samples have higher Co, Cr and Ni values than the average for serpentinite (Uçurum, 1996). Edel'shteyn and Pilipenko (1978) report that Co and Ni behave inertly during serpentinization and are redistributed only locally between silicate and oxide phases. During this redistribution Co and Ni may enrich randomly and locally. In addition, apparent Co, Cr and Ni enrichment in serpentinite from the Divriği and Hekimhan regions is perhaps a result of limited sampling of serpentinite in these study areas. Barium is enriched in silica-carbonate (type I) listwaenites than in asso-

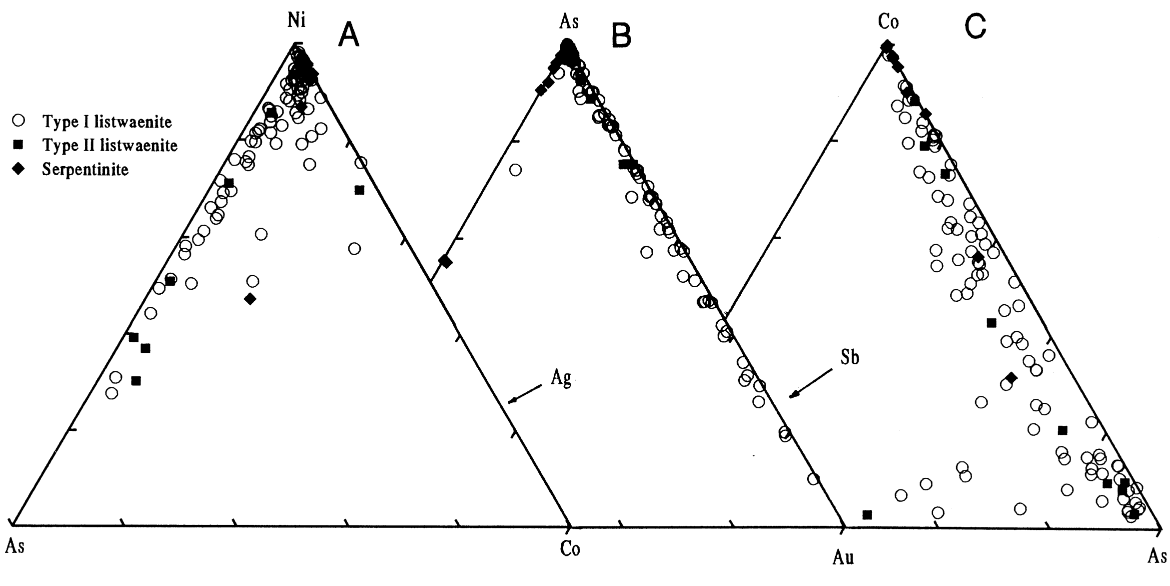



Fig. 7 - Ternary diagrams for listwaenites and serpentinites from Divriği and Hekimhan regions. Data are from Table 3. A) Ni-As-Co, B) Ag-As-Au, C) Ni-As-Co diagrams.

ciated type II listwaenites and serpentinites.

Figs. 7a, 7b and 7c show that Co-As, Ni-As and Au-As are closely associated in listwaenites and serpentinite and were probably in equilibrium in hydrothermal solution during alteration of the mafic-ultramafic rocks. Close association between Co-As, Ni-As and Au-As suggest that those elements were in equilibrium in the hydrothermal fluids and introduced as arsenic complexes. Concentrations of Au and Ag are generally very low in both types of listwaenites, although local anomalies have been detected in the Güvenç and Karakuz areas. Neither Sb and Ag are associated with As, and this suggests that Sb and Ag were introduced into the system by hydrothermal fluids in low concentrations. Clear Co, Ni and Au associations with As in the listwaenites suggest that the these metals were brought into the system by hydrothermal fluids during the listwaenitization of serpentinite.

As, Ba, Zn and Sb are enriched in listwaenite with respect to associated serpentinite in the Divriği-Hekimhan district. Presence and amount of Si in the hydrothermal fluid were probably important in determining base and precious metal contents in the listwaenites, because silica-carbonate listwaenite is enriched in As, Ba, Co, Cr, Ni, Zn and Sb when compared to carbonate listwaenite.

Analysis of La, Ce, Nd, Sm, Eu, Yb and Lu are presented in Table 4. REEs are enriched in both listwaenites and serpentinite with respect to chondrite (Fig. 8a). Both figures show that serpentinites have the highest concentration of REEs followed by carbonate listwaenite and silica-carbonate listwaenite. MORB normalized patterns (Fig. 8b) of listwaenites and associated rock units have negative slopes from La to Yb. Neodymium, Sm, Eu and Yb patterns of both silica-carbonate and carbonate listwaenites are below the average MORB line and only La enriched in those rock units. Ce is slightly negative in silica-carbonate listwaenite and slightly positive in carbonate listwaenite (Figs. 8a, 8b). Sm anomalies present slightly negative in serpentinite and in listwaenites, however Eu is slightly positive only in serpentinite and slightly negative in other rock units (Figs. 9a, 9b). Negative Ce anomalies are good evidence of equilibration with sea water with a REE pattern similar to the modern sea water. Fryer (1977a; 1977b) has shown that chondrite-normalized REE patterns in ocean-ridge sediments, including metaliferous ones, show small negative Eu anomalies and deep negative Ce anomalies. These patterns suggest that silica-carbonate listwaenites in the Divrigi and Hekimhan regions were formed by hydrothermal fluids with slight interaction with sea water, because the Ce pattern of silica-carbonate listwaenites is not strongly negative enough to represent only a sea water signature. Serpentinite bodies in the Divriği-Hekimhan region with (Fig. 8b) slightly positive Ce anomalies (Figs. 8a, 8b), suggests that the serpentinization of mafic-ultramafic rocks in the Kuluncak and Divrigi melanges occurred on land after obduction was completed. Carbonate listwaenite formed by meteoric water hydrothermal fluids.

Normal MORB normalized REE patterns (Fig. 8b) of the listwaenites and associated serpentinite show that Nd in listwaenites, Sm and Eu in serpentinite and listwaenites and Yb in all rock units are below average MORB values. This pattern may indicate that the origin of these alteration products is related to depleted MORB (Wilson, 1989). In other words, the parent rocks of listwaenites and serpentinite were derived from ultramafic rocks which originated in a mid-oceanic ridge environment from slightly REE depleted magma with respect to MORB. Mid-oceanic ridge basalt, and chondrite normalized REE patterns of both types of listwaenites and serpentinite show that the listwaenites and serpentinite are genetically related in that listwaenite is derived from serpentinite by its reaction with hydrothermal fluids. The source rocks for listwaenites and serpentinite were from slightly REE depleted MORB.

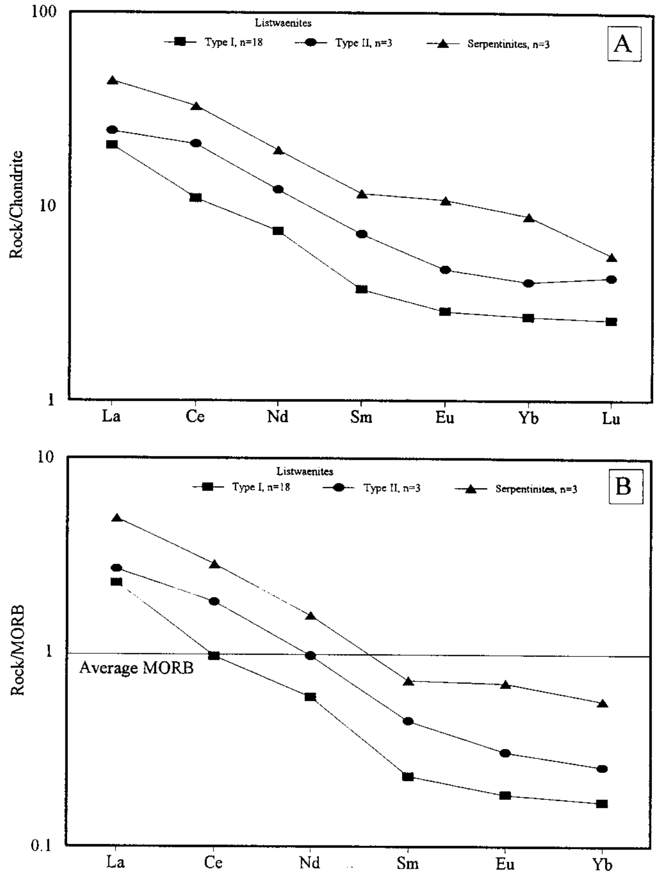



Fig. 8 - Rare-earth element patterns of listwaenites and serpentinites in the Divriği and Hekimhan regions. Data are from Table 4 (1996). A) Chondrite normalized, normalizing constants are from Nakamura (1974). B) Mid-Oceanic Ridge Basalt normalized, normalizing constants are from Bevins et al., (1984), and Pearce (1983).

The REE patterns in all listwaenite samples suggest a relatively immobile behavior of the REEs during alteration. The general lowering of the REE concentrations in the listwaenites can be best explained by a mass increase in the altered rocks due to addition of chemical components during this process.

## Listwaenitization Processes

Listwaenitization occur in the shear, thrust and faulted-fractured porous zones of ultramafic rocks which act as pathways for altering and mineralizing fluids. Silica-carbonate alteration and development of listwaenites post-date serpentinization of ultramafic complexes.

Listwaenite bodies in the Güvenç, Karakuz and Cürek areas are (Figs. 2, 3, 4) formed by means of several chemical changes in serpentinites from the Divriği (Divriği-Sivas) and Kuluncak ophiolitic mélanges (Hekimhan-Malatya). Silica-carbonate listwaenite is an early alteration product and is followed by carbonate listwaenite which formed as a final product from the alteration of serpentinized ultramafic rocks. Major oxide chemical analyses show that addition of calcium, carbon dioxide, and silica, and removal of magnesium oxide characterize the change from serpentinite to sili-

Table 3 - Base and precious metal concentrations of the listwaenites and associated alteration products of ultramafic rocks in the Divriği-Hekimhan region

| **Analytical method** | | **INAA** | **ICP** | **INAA** | **INAA** | **INAA** | **INAA** | **ICP** | **ICP** | **ICP** | **ICP** | **INAA** | **INAA** | **ICP** | **ICP** | **ICP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Element** | | **Au** | **Ag** | **As** | **Ba** | **Co** | **Cr** | **Ni** | **Zn** | **Pb** | **Cu** | **Sb** | **Sc** | **Sr** | **V** | **Y** |
| **Unit** | | **ppb** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** | **ppm** |
| **Detection limit** | | **2** | **0.4** | **0.5** | **50** | **1** | **5** | **1** | **1** | **5** | **1** | **0.1** | **0.1** | **1** | **2** | **2** |
| | **Sample #s** | | | | | | | | | | | | | | | |
| **Type I-------------** | ADG-1 | 5 | 0.2 | 26 | 630 | 1 | 11 | 68 | 422 | 164 | 8 | 1.2 | 0.5 | 46 | 4 | 8 |
| **Listwaenite** | ADG-2 | 23 | 30.4 | 1700 | 19000 | 80 | 1700 | 1408 | 37354 | 2238 | 82 | 31 | 5.6 | 337 | 11 | 5 |
| | ADG-3 | 6 | 0.2 | 5.5 | 25 | 21 | 1800 | 537 | 39 | 6 | 4 | 2 | 4.7 | 73 | 9 | 2 |
| | ADG-4 | 13 | 0.2 | 3.1 | 25 | 38 | 3300 | 1066 | 12 | 2.5 | 2 | 0.5 | 1.7 | 82 | 2 | 1 |
| | ADG-5 | 6 | 0.2 | 4.1 | 100 | 23 | 2000 | 1329 | 11 | 2.5 | 7 | 1.8 | 5.2 | 81 | 11 | 1 |
| | ADG-6 | 3 | 0.2 | 5.2 | 79 | 1 | 19 | 24 | 8 | 5 | 6 | 0.7 | 0.8 | 44 | 3 | 14 |
| | ADG-6A | 20 | 0.8 | 430 | 130 | 38 | 1700 | 685 | 16 | 15 | 57 | 9 | 10 | 119 | 33 | 8 |
| | ADG-8 | 3 | 0.2 | 16 | 110 | 29 | 3600 | 1552 | 23 | 2.5 | 5 | 0.7 | 2.9 | 72 | 2 | 2 |
| | ADG-9 | 1 | 2.9 | 1600 | 1200 | 110 | 1800 | 3327 | 254 | 362 | 3099 | 65 | 5.5 | 103 | 9 | 2 |
| | ADG-10 | 25 | 0.2 | 34 | 1000 | 20 | 1900 | 419 | 26 | 5 | 6 | 1.3 | 4.6 | 140 | 8 | 1 |
| | ADG-13 | 1 | 0.2 | 120 | 180 | 35 | 1500 | 868 | 182 | 35 | 48 | 2.3 | 4.7 | 135 | 11 | 7 |
| | ADG-14 | 7 | 0.2 | 7.6 | 280 | 79 | 1900 | 675 | 43 | 9 | 13 | 4 | 5.3 | 76 | 12 | 1 |
| | ADG-15 | 3 | 9.8 | 200 | 80 | 31 | 2400 | 234 | 11 | 68 | 32 | 3 | 0.7 | 6 | 4 | 1 |
| | ADG-16 | 18 | 0.2 | 16 | 240 | 20 | 3200 | 295 | 20 | 2.5 | 3 | 5.3 | 3.1 | 130 | 4 | 2 |
| | ADG-17 | 1 | 0.2 | 1.6 | 120 | 5 | 110 | 9 | 24 | 2.5 | 4 | 0.05 | 18 | 175 | 2 | 8 |
| | ADG-18 | 14 | 0.2 | 29 | 180 | 41 | 1900 | 1136 | 468 | 35 | 6 | 4.2 | 5 | 157 | 10 | 1 |
| | ADG-19 | 8 | 1.2 | 20 | 96 | 180 | 1700 | 3100 | 747 | 127 | 8 | 3.6 | 2.3 | 53 | 4 | 1 |
| | ADG-23 | 10 | 0.2 | 7.4 | 500 | 57 | 1800 | 1350 | 17 | 7 | 17 | 2.8 | 4.8 | 51 | 9 | 1 |
| | ADG-24 | 1 | 0.2 | 170 | 25 | 26 | 3100 | 446 | 16 | 2.5 | 7 | 2.4 | 48 | 128 | 107 | 1 |
| | ADG-25 | 17 | 0.2 | 49 | 25 | 34 | 1300 | 778 | 22 | 2.5 | 22 | 5.2 | 4.7 | 122 | 8 | 1 |
| | ADG-26 | 5 | 2.5 | 1500 | 70 | 81 | 1800 | 1659 | 187 | 7 | 1167 | 990 | 4.4 | 38 | 8 | 2 |
| | ADG-27 | 10 | 0.4 | 870 | 130 | 37 | 1800 | 1258 | 64 | 21 | 29 | 20 | 5.6 | 85 | 9 | 1 |
| | ADG-28 | 26 | 0.2 | 2.9 | 25 | 33 | 780 | 1108 | 30 | 7 | 3 | 0.3 | 2.4 | 500 | 9 | 1 |
| | ADG-29 | 5 | 0.2 | 4.6 | 25 | 39 | 1700 | 519 | 12 | 2.5 | 4 | 0.4 | 2.2 | 199 | 2 | 1 |
| | ADG-34 | 6 | 0.2 | 610 | 140 | 84 | 2700 | 1261 | 38 | 20 | 79 | 52 | 2.4 | 85 | 5 | 4 |
| | ADG-35 | 11 | 0.2 | 500 | 210 | 33 | 2000 | 1674 | 39 | 9 | 63 | 45 | 2.2 | 76 | 4 | 2 |
| | ADG-35A | 4 | 0.6 | 26 | 120 | 4 | 57 | 130 | 19 | 10 | 19 | 2 | 0.4 | 37 | 9 | 28 |
| | ADG-36 | 5 | 1.7 | 220 | 60 | 13 | 91 | 301 | 125 | 25 | 20 | 4.4 | 5.1 | 56 | 12 | 11 |
| | ADG-37 | 4 | 0.2 | 5.7 | 82 | 3 | 300 | 33 | 16 | 8 | 8 | 1.3 | 0.8 | 60 | 3 | 11 |
| | ADG-38 | 5 | 0.6 | 53 | 25 | 64 | 1400 | 639 | 37 | 11 | 22 | 14 | 6 | 98 | 10 | 5 |
| | ADG-39 | 15 | 0.2 | 21 | 1400 | 4 | 24 | 81 | 31 | 6 | 11 | 0.9 | 1.8 | 125 | 2 | 16 |
| | ADG-40 | 11 | 0.2 | 10 | 25 | 4 | 35 | 84 | 27 | 2.5 | 4 | 1.5 | 0.6 | 61 | 2 | 12 |
| | ADG-41 | 20 | 0.5 | 9.5 | 70 | 51 | 3800 | 1481 | 58 | 8 | 7 | 1.6 | 3.3 | 114 | 6 | 1 |
| | ADG-42 | 7 | 2.2 | 140 | 420 | 76 | 3600 | 223 | 60 | 17 | 38 | 14 | 1.9 | 14 | 13 | 1 |
| | ADG-44 | 6 | 0.2 | 2.2 | 260 | 9 | 580 | 287 | 13 | 2.5 | 24 | 0.2 | 45 | 10 | 72 | 10 |
| | ADG-46 | 1 | 5.9 | 1000 | 25 | 94 | 4500 | 1730 | 5 | 15 | 56 | 0.8 | 2.5 | 86 | 2 | 2 |
| | ADG-58 | 72 | 0.8 | 18 | 13000 | 38 | 750 | 354 | 19 | 6 | 4 | 3.9 | 3.4 | 263 | 7 | 2 |
| | ADG-60 | 3 | 0.2 | 3.5 | 290 | 230 | 2700 | 712 | 9 | 2.5 | 17 | 1.8 | 4.7 | 169 | 4 | 2 |
| | ADK-22 | 1 | 0.2 | 69 | 25 | 26 | 3000 | 416 | 114 | 26 | 66 | 8.9 | 4 | 188 | 2 | 1 |
| | ADK-24 | 1 | 0.2 | 57 | 25 | 34 | 2900 | 441 | 42 | 33 | 4 | 6.3 | 1.7 | 11 | 11 | 1 |
| | ADK-25 | 1 | 0.2 | 190 | 150 | 34 | 2000 | 686 | 150 | 121 | 17 | 8.5 | 3.1 | 218 | 2 | 1 |
| | ADK-26 | 6 | 0.2 | 27 | 200 | 29 | 9000 | 332 | 36 | 16 | 6 | 0.6 | 1.6 | 163 | 2 | 1 |
| | ADK-27 | 1 | 0.2 | 47 | 280 | 72 | 1600 | 1130 | 138 | 35 | 4 | 3.1 | 3.9 | 70 | 5 | 1 |
| | ADK-41 | 1 | 6 | 20 | 150 | 34 | 1500 | 475 | 35 | 22 | 193 | 8.4 | 4.2 | 64 | 12 | 2 |
| | ADC-1 | 7 | 0.2 | 35 | 68 | 45 | 1600 | 943 | 57 | 2.5 | 115 | 5.1 | 3.6 | 90 | 11 | 1 |
| | ADC-2 | 15 | 0.2 | 240 | 25 | 33 | 2300 | 1070 | 31 | 8 | 31 | 14 | 3.6 | 23 | 8 | 1 |
| | ADC-3 | 18 | 0.2 | 140 | 1500 | 30 | 2900 | 505 | 39 | 20 | 56 | 19 | 5.5 | 74 | 16 | 6 |
| | ADC-4 | 35 | 0.2 | 85 | 74 | 63 | 2900 | 1082 | 25 | 10 | 15 | 9.8 | 4 | 159 | 10 | 1 |
| | ADC-5 | 6 | 0.2 | 37 | 260 | 52 | 1400 | 1510 | 17 | 2.5 | 6 | 1.7 | 4.5 | 229 | 7 | 1 |
| | ADC-6 | 8 | 0.2 | 15 | 1000 | 2 | 250 | 30 | 3 | 2.5 | 1 | 13 | 0.2 | 20 | 3 | 1 |
| | ADC-7 | 1 | 0.5 | 42 | 25 | 39 | 2400 | 1004 | 22 | 2.5 | 3 | 4.9 | 5 | 51 | 25 | 1 |
| | ADC-8 | 16 | 0.2 | 28 | 110 | 77 | 2300 | 2052 | 9 | 2.5 | 3 | 7 | 2.8 | 219 | 2 | 1 |
| | ADC-9 | 1 | 0.2 | 41 | 99 | 52 | 1500 | 887 | 47 | 2.5 | 6 | 9.4 | 3.4 | 43 | 10 | 1 |
| | ADC-10 | 6 | 0.2 | 22 | 25 | 55 | 2800 | 1158 | 17 | 2.5 | 29 | 3.9 | 7.2 | 69 | 10 | 1 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ADC-11 | 1 | 0.4 | 13 | 350 | 44 | 1800 | 266 | 21 | 2.5 | 26 | 3.6 | 4.4 | 24 | 7 | 1 |
| | ADC-12 | 23 | 2.8 | 150 | 25 | 82 | 860 | 357 | 88 | 32 | 62 | 15 | 35 | 21 | 144 | 4 |
| | ADC-13 | 26 | 0.2 | 11 | 23000 | 2 | 330 | 60 | 8 | 8 | 4 | 5.5 | 0.4 | 400 | 4 | 1 |
| | ADC-14 | 1 | 0.2 | 98 | 25 | 10 | 2300 | 242 | 328 | 83 | 65 | 16 | 4 | 12 | 9 | 1 |
| | ADC-15 | 14 | 0.2 | 31 | 1300 | 15 | 2200 | 495 | 41 | 12 | 106 | 11 | 4.4 | 50 | 9 | 1 |
| | ADC-16 | 6 | 0.2 | 17 | 25 | 50 | 1400 | 1127 | 19 | 6 | 12 | 1.4 | 4 | 208 | 9 | 1 |
| | ADC-17 | 1 | 0.2 | 17 | 25 | 77 | 2000 | 1446 | 21 | 2.5 | 27 | 0.6 | 4.6 | 135 | 9 | 1 |
| | ADC-18 | 1 | 0.2 | 39 | 100 | 29 | 1100 | 819 | 213 | 44 | 5 | 6.3 | 3.4 | 129 | 10 | 1 |
| | ADC-19 | 1 | 0.2 | 34 | 25 | 150 | 2000 | 3328 | 74 | 30 | 10 | 0.8 | 4.5 | 116 | 8 | 1 |
| | ADC-20 | 1 | 0.2 | 45 | 25 | 41 | 1500 | 1517 | 17 | 2.5 | 10 | 2.4 | 4.8 | 114 | 7 | 1 |
| | ADC-21 | 1 | 0.4 | 11 | 25 | 63 | 1800 | 2752 | 21 | 2.5 | 23 | 1.2 | 4.1 | 210 | 7 | 1 |
| | ADC-22 | 9 | 0.4 | 20 | 160 | 38 | 1500 | 572 | 33 | 2.5 | 3 | 7.9 | 4.6 | 67 | 12 | 1 |
| | ADC-23 | 10 | 0.2 | 29 | 25 | 57 | 1800 | 1004 | 12 | 7 | 11 | 2.1 | 1.6 | 23 | 6 | 1 |
| | ADC-24 | 7 | 0.2 | 19 | 58 | 30 | 2400 | 2228 | 99 | 6 | 7 | 4.8 | 5 | 98 | 7 | 1 |
| | ADC-25 | 13 | 0.2 | 9.1 | 25 | 40 | 1500 | 1087 | 15 | 2.5 | 5 | 0.7 | 1.9 | 74 | 5 | 1 |
| | ADC-26 | 8 | 0.2 | 13 | 54 | 58 | 2100 | 2288 | 18 | 2.5 | 3 | 0.7 | 2.4 | 321 | 2 | 1 |
| | ADC-27 | 7 | 0.2 | 160 | 120 | 30 | 1100 | 1214 | 47 | 9 | 8 | 12 | 4 | 35 | 52 | 4 |
| | ADC-28 | 11 | 0.2 | 55 | 130 | 12 | 3200 | 414 | 56 | 12 | 9 | 28 | 4.1 | 7 | 16 | 1 |
| | ADC-29 | 3 | 0.2 | 29 | 89 | 9 | 2100 | 194 | 24 | 10 | 7 | 5.5 | 2.3 | 6 | 7 | 1 |
| | ADC-30 | 1 | 0.2 | 1500 | 150 | 42 | 3400 | 1502 | 137 | 99 | 42 | 65 | 5.8 | 17 | 79 | 5 |
| | ADC-31 | 6 | 0.2 | 18 | 25 | 35 | 1700 | 222 | 14 | 2.5 | 5 | 3.4 | 2.9 | 7 | 3 | 1 |
| | ADC-32 | 14 | 0.2 | 310 | 25 | 53 | 13000 | 1632 | 270 | 48 | 53 | 220 | 15 | 7 | 85 | 2 |
| | ADC-33 | 13 | 0.2 | 72 | 340 | 4 | 45 | 29 | 11 | 15 | 18 | 23 | 0.8 | 33 | 42 | 2 |
| | ADC-34 | 1 | 0.2 | 29 | 25 | 62 | 2000 | 1228 | 15 | 5 | 4 | 1.2 | 5.9 | 109 | 6 | 1 |
| | ADC-35 | 6 | 0.2 | 57 | 1900 | 79 | 3100 | 1018 | 92 | 12 | 5 | 8 | 2.5 | 47 | 11 | 1 |
| | ADC-43 | 9 | 0.2 | 15 | 430 | 31 | 1800 | 681 | 32 | 7 | 97 | 3.8 | 4.6 | 58 | 8 | 1 |
| | ADC-45 | 8 | 0.2 | 18 | 120 | 31 | 2200 | 793 | 16 | 2.5 | 18 | 2.1 | 3.2 | 51 | 4 | 1 |
| | ADC-46 | 13 | 0.2 | 27 | 180 | 45 | 1400 | 985 | 22 | 5 | 21 | 1.6 | 2.7 | 213 | 12 | 1 |
| | ADC-47 | 1 | 0.2 | 47 | 110 | 2 | 28 | 22 | 7 | 2.5 | 43 | 2 | 5.3 | 49 | 38 | 7 |
| | ADC-49 | 7 | 0.2 | 490 | 280 | 58 | 3600 | 1124 | 41 | 2.5 | 63 | 13 | 7.1 | 31 | 12 | 1 |
| | ADC-53 | 5 | 0.2 | 2.3 | 100 | 3 | 12 | 20 | 8 | 2.5 | 1 | 0.4 | 2.3 | 11 | 11 | 5 |
| | ADC-54 | 12 | 0.2 | 6.4 | 230 | 10 | 260 | 49 | 35 | 6 | 39 | 1 | 8 | 27 | 33 | 10 |
| | *Average* | *8.15* | *0.63* | *81.82* | *213.48* | *37.32* | *1861.67* | *718.53* | *68.08* | *17.47* | *25.14* | *8.13* | *5.31* | *100.08* | *14.55* | *3.08* |
| **Type II------------ Listwaenite** | ADG-30 | 9 | 0.2 | 28 | 25 | 8 | 54 | 212 | 238 | 44 | 9 | 2.9 | 2.7 | 260 | 11 | 4 |
| | ADG-31 | 2 | 0.2 | 6.7 | 360 | 6 | 23 | 182 | 24 | 8 | 5 | 1.3 | 0.7 | 52 | 4 | 4 |
| | ADG-32 | 5 | 0.7 | 45 | 25 | 5 | 24 | 123 | 21 | 10 | 9 | 2.6 | 1.9 | 34 | 8 | 7 |
| | ADG-67 | 1 | 0.2 | 16 | 93 | 49 | 1900 | 1053 | 22 | 2.5 | 3 | 1.7 | 1.8 | 44 | 4 | 1 |
| | ADK-35 | 37 | 2.3 | 120 | 25 | 4 | 17 | 80 | 521 | 414 | 15 | 4.1 | 0.7 | 46 | 3 | 2 |
| | ADK-36 | 1 | 1.8 | 88 | 25 | 5 | 28 | 96 | 406 | 324 | 155 | 98 | 0.8 | 35 | 3 | 4 |
| | ADK-37 | 1 | 1.5 | 89 | 130 | 8 | 19 | 57 | 587 | 294 | 42 | 2.9 | 1.2 | 27 | 8 | 2 |
| | ADK-38 | 1 | 0.8 | 110 | 120 | 12 | 8 | 53 | 572 | 235 | 12 | 2.1 | 0.5 | 26 | 4 | 2 |
| | ADK-39 | 1 | 0.2 | 41 | 25 | 330 | 2700 | 857 | 150 | 166 | 21 | 2.8 | 1.6 | 102 | 7 | 2 |
| | ADK-48 | 1 | 0.2 | 15 | 25 | 68 | 1500 | 1136 | 108 | 39 | 6 | 3 | 4.2 | 335 | 7 | 2 |
| | *Average* | *2.44* | *0.81* | *48.74* | *85.30* | *18.33* | *24.71* | *114.71* | *22.33* | *20.70* | *13.55* | *2.6* | *1.61* | *96.10* | *5.90* | *3.00* |
| **Serpentinite------** | ADG-12 | 4 | 0.2 | 0.25 | 25 | 91 | 4700 | 2027 | 35 | 2.5 | 12 | 0.4 | 4.6 | 1 | 8 | 1 |
| | ADG-33 | 1 | 0.2 | 60 | 1700 | 33 | 27 | 83 | 154 | 33 | 16 | 12 | 20 | 382 | 185 | 26 |
| | ADG-43 | 14 | 0.2 | 8.6 | 60 | 89 | 2500 | 1349 | 23 | 2.5 | 77 | 1.3 | 5.8 | 6 | 12 | 1 |
| | ADG-45 | 1 | 0.2 | 0.25 | 110 | 140 | 5500 | 2055 | 21 | 2.5 | 49 | 0.05 | 16 | 2 | 23 | 1 |
| | ADG-57 | 12 | 0.6 | 26 | 190 | 38 | 2300 | 417 | 9 | 2.5 | 2 | 3.4 | 2.5 | 112 | 4 | 2 |
| | ADG-66 | 1 | 0.2 | 5 | 25 | 30 | 1900 | 416 | 18 | 2.5 | 107 | 0.05 | 39 | 94 | 85 | 5 |
| | ADK-33 | 1 | 0.2 | 3.8 | 25 | 83 | 3800 | 1978 | 15 | 5 | 5 | 0.3 | 5 | 4 | 5 | 2 |
| | ADC-52 | 16 | 0.2 | 2.5 | 25 | 94 | 2300 | 2395 | 19 | 2.5 | 5 | 0.3 | 11 | 3 | 30 | 1 |
| | ADC-58 | 1 | 0.2 | 1.9 | 25 | 82 | 2200 | 1741 | 31 | 5 | 20 | 0.2 | 9.4 | 3 | 34 | 2 |
| | *Average* | *5.66* | *0.24* | *12.03* | *60.62* | *67.50* | *2803.00* | *1384.56* | *21.37* | *6.44* | *23.25* | *2.00* | *12.59* | *67.44* | *42.89* | *4.56* |

ADG = Güvenç; ADK = Karakuz; ADC = Cürek.

Concentration values of some elements are accepted as a half of the detection limit. Those elements are originally reported by ACTLAB below the detection limit of analytical instruments. Underlined values are excluded from average values.

Table 4 - Rare-Earth element concentrations of the listwaenites and adjacent rock units from ophiolitic melanges in Hekimhan and Divriği regions

| Analytical method | | INAA | INAA | INAA | INAA | INAA | INAA | INAA |
|---|---|---|---|---|---|---|---|---|
| Element | | **La** | **Ce** | **Nd** | **Sm** | **Eu** | **Yb** | **Lu** |
| Unit | | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Detection limit | | 0.5 | 3 | 5 | 0.1 | 0.2 | 0.2 | 0.05 |
| | Sample #s | | | | | | | |
| **Type I--------------** | ADG-6 | 2.9 | 4 | 2.5 | 0.9 | 0.3 | 1.2 | 0.15 |
| **listwaenite** | ADG-6A | 1 | 5 | 2.5 | 0.6 | 0.1 | 1.1 | 0.17 |
| | ADG-13 | 1.5 | 6 | 2.5 | 0.6 | 0.1 | 0.6 | 0.08 |
| | ADG-16 | 7.3 | 8 | 2.5 | 0.2 | 0.1 | 0.3 | 0.05 |
| | ADG-26 | 1.2 | 3 | 13 | 0.2 | 0.1 | 0.1 | 0.025 |
| | ADG-34 | 3.6 | 8 | 2.5 | 0.5 | 0.3 | 0.3 | 0.025 |
| | ADG-35 | 2.5 | 5 | 2.5 | 0.4 | 0.3 | 0.3 | 0.06 |
| | ADG-37 | 7.8 | 5 | 8 | 1.6 | 0.4 | 0.9 | 0.13 |
| | ADG-38 | 0.7 | 4 | 2.5 | 0.4 | 0.1 | 0.4 | 0.06 |
| | ADG-39 | 9.2 | 6 | 8 | 2.3 | 0.6 | 1.7 | 0.23 |
| | ADG-40 | 4.6 | 3 | 2.5 | 0.9 | 0.2 | 1 | 0.17 |
| | ADG-58 | 43 | 31 | 2.5 | 0.3 | 0.4 | 0.3 | 0.025 |
| | ADC-3 | 3.7 | 8 | 5 | 0.4 | 0.1 | 0.4 | 0.07 |
| | ADC-27 | 2.1 | 1.5 | 2.5 | 0.3 | 0.1 | 0.4 | 0.07 |
| | ADC-32 | 1.2 | 5 | 2.5 | 0.3 | 0.1 | 0.1 | 0.11 |
| | ADC-33 | 23 | 53 | 14 | 1.8 | 0.3 | 0.5 | 0.025 |
| | ADC-47 | 1.8 | 4 | 2.5 | 0.8 | 0.1 | 0.4 | 0.05 |
| | ADC-53 | 5.6 | 12 | 7 | 1.2 | 0.3 | 0.7 | 0.09 |
| | **Average** | **6.82** | **9.53** | **4.72** | **0.76** | **0.22** | **0.59** | **0.09** |
| **Type II-------------** | ADC-54 | 21 | 50 | 18 | 3.9 | 0.9 | 2 | 0.28 |
| **listwaenite** | ADG-30 | 1 | 1.5 | 2.5 | 0.3 | 0.1 | 0.3 | 0.06 |
| | ADG-31 | 2.2 | 3 | 2.5 | 0.2 | 0.1 | 0.4 | 0.1 |
| | **Average** | **8.07** | **18.17** | **7.67** | **1.47** | **0.37** | **0.9** | **0.15** |
| **Serpentinite-------** | ADG-32 | 2.8 | 3 | 2.5 | 0.3 | 0.1 | 1.4 | 0.21 |
| | ADG-33 | 41 | 81 | 32 | 6.5 | 2.2 | 3.9 | 0.34 |
| | ADG-66 | 0.25 | 1.5 | 2.5 | 0.3 | 0.2 | 0.6 | 0.025 |
| | **Average** | **14.68** | **28.5** | **12.33** | **2.37** | **0.83** | **1.97** | **0.19** |

ADG = Güvenç; ADK = Karakuz; ADC = Cürek. REEs are determined by INAA.
Concentration values of some elements are accepted as a half of the detection limit. Those elements are originally reported by ACTLAB below the detection limit of analytical instruments.

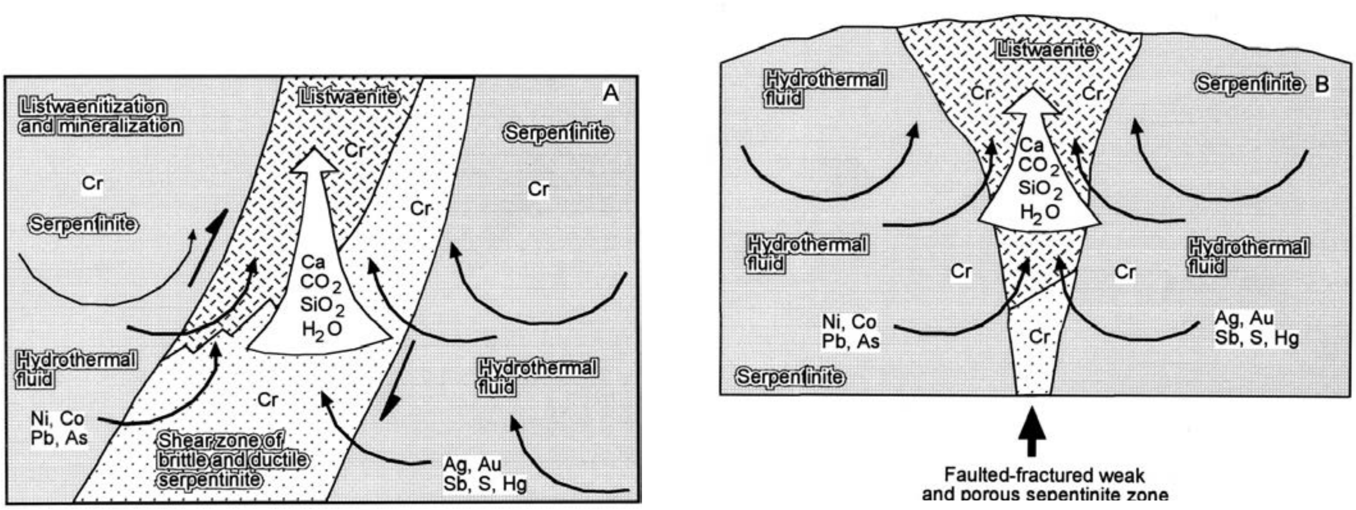



Fig. 9 - Suggested model for listwaenitization and mineralization in the Divriği-Hekimhan region. A) Thrust fault related model, B) Non-thrust fault related model. When carbonate listwaenite is subject to this model, silica is considered to be absent from the hydrothermal fluids (Uçurum, 1996).

ca-carbonate listwaenites. The resulting rock is silica-carbonate dominated with relics of serpentinite and chromitite fragments. Silica-carbonate listwaenite, the latest product of listwaenitization in the Divriği and Hekimhan districts, is characterized by the introduction of calcium, and carbon dioxide and removal of magnesium oxide and silica.

Listwaenitization occurs by metasomatism of weakly serpentinized or completely serpentinized mafic minerals or by hydrothermal alteration of serpentinized mafic minerals or by combination of both processes. Although Capedri and Rossi (1973) report that listwaenite bodies are derived from fresh ultramafic rocks in central Euboea, Greece, most investigations show listwaenite to be later than serpentinization and to be superimposed on the earlier serpentinite (Ploshko, 1963; Scherban and Borovikova, 1970; Zhelobov, 1979; Kashkai and Allakhverdiev, 1965; Spirdinow, 1991; Schandl and Naldrett, 1992).

Listwaenite can form by the following chemical reactions from serpentinites:

(*i*) When both $CO_2$ and CaO act directly on serpentine minerals, the process can directly form listwaenite;

$$\underset{\text{serpentine}}{Mg_3Si_2O_8(OH)_4} + \underset{\text{added}}{CaO + 4CO_2} \rightarrow \underbrace{\underline{\underset{\text{magnesite}}{2MgCO_3} + \underset{\text{dolomite}}{CaMg(CO_3)_2} + \underset{\text{quartz}}{4SiO_2}}}_{\text{silica-carbonate listwaenite}} + H_2O$$

(*ii*) However, if only carbon dioxide directly affects the serpentinites then magnesite+quartz listwaenitic rocks form;

$$\underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} + \underset{\text{added}}{3CO_2} \rightarrow \underset{\text{magnesite}}{3MgCO_3} + \underset{\text{quartz}}{2SiO_2} + 2H_2O$$

(*iii*) Carbonate listwaenites lack any significant silica and are probably formed by dissolving of $SiO_2$ at high pH and moderately high temperature conditions in the hydrothermal fluid, because $SiO_2$ is more soluble at high pH (≥ 9) and the solubility of Ca increases with decreasing temperature (25-60 $^0$C) with low partial pressures of $CO_2$ ($3x10^{-4}$ atm) (Faure, 1991). Chemical reactions for this type listwaenite formation from serpentinites could be:

$$\underset{\text{serpentine}}{Mg_3Si_2O_8(OH)_4} + \underset{\text{added}}{CaO + 4CO_2} \text{ Æ } \underbrace{\underline{\underset{\text{magnesite}}{2MgCO_3} + \underset{\text{dolomite}}{CaMg(CO_3)_2}}}_{\text{carbonate listwaenite}} + \underset{\text{removed}}{4SiO_2} + H_2O$$

## Genesis of listwaenites

Formation models for the listwaenite bodies from the Divriği and Kuluncak ophiolitic mélanges, based primarily on alteration assemblages and element associations, is summarized in Fig. 9 a and b. The model invokes two main listwaenite-forming events, thrust fault related and non-thrust fault related listwaenitization. Genetically there are no significant differences between the two different settings.

All of the silica-carbonate, and some of carbonate listwaenites in the Cürek (Fig. 2) Güvenç (Fig. 3), and Karakuz (Fig. 4) areas formed along the major and minor thrust faults inside or bordering serpentinized ultramafic rocks. Thrust fault zones acted as pathways for hydrothermal fluids (Fig. 9a). Almost all of the silica-carbonate listwaenite in Cürek (Fig. 2) and the carbonate listwaenite in the Güvenç area (Fig. 3), however, seem to have formed by non-thrust fault related processes. In this type of listwaenite alteration the mineralizing fluids are considered to pass through a porous and weak (including a number of small scale cracks and faults) and highly altered serpentinite zone (Fig. 9b).

As is evidenced by remnant serpentinite fragments within listwaenite bodies, formation of listwaenites took place after serpentinization was completed in ophiolitic mélanges. Silica-carbonate (type I) listwaenite formation was initiated by the development of micro-crystalline cristobalite and quartz due to removal of silica from serpentinites. A minor amount of carbonate also was early. When $SiO_2$, $CO_2$ and Ca were introduced into the system by hydrothermal fluids, macro-crystalline quartz, calcite, dolomite and ankerite precipitated from hydrothermal fluids. In carbonate (type II) listwaenites silica is absent or present in very small quantities in the hydrothermal fluids. Silica is present basically in a micro crystalline form with a very minor amount of macro crystalline quartz.

Introduction of Ca, $CO_2$, $SiO_2$, and the addition of As, Ag, Ba, Zn, Co, Ni and Sb into serpentinized ultramafic rock or, subsequently, into silica-carbonate (type I) listwaenite suggest an acidic nature for the hydrothermal fluids responsible for the chemical changes of serpentinite. However, during the formation of carbonate (type II) listwaenite, Ca, $CO_2$, As, Ag, Ba, and Pb are introduced into serpentinites while significant amount of silica is lacking. This suggests that the fluid evolves and changes in composition due to wall rock interaction or that two chemically different hydrothermal fluids affected the formation of different listwaenites in the Divriği and Hekimhan districts. Absence of silica in the hydrothermal fluid for carbonate listwaenite results from one or a combination of the following reasons; lack of silica source, high pH (9 or more) fluid environment which retains Si in solution, lower oxygen fugacity or lower temperature.

Neither silica-carbonate or carbonate listwaenites carry any economic concentrations of Au or Ag in any of the study areas, although Au contents of up to 72 ppb in Güvenç and up to 37 ppb in Karakuz and Ag contents of up to 30 ppm in Güvenç (Uçurum, 1996) are sufficiently high as to warrant additional exploration. Base and precious metal concentrations are generally higher in silica-carbonate listwaenite than in carbonate listwaenite. This may suggest that additional silica in the silica-carbonate hydrothermal solutions is the major factor that controlled the concentrations of minor elements in hydrothermal fluids.

Hydrothermal fluids were enriched in Si, Ca, Pb, Ag, As, and Ba. Gold and sulfide complexes were probably derived from the ultramafic lithologies in a manner similar to that described by Buisson and Leblanc (1985, 1986).

The silica-carbonate listwaenites were formed from a meteoric hydrothermal fluid, enriched in $SiO_2$, $CO_2$, $H_2O$ and Ca, characterized by low pH and low to moderate temperature (150-300 $^0$C; Uçurum, 1996). They formed along thrust faults, and within highly serpentinized porous ultramafic zones. The meteoric hydrothermal fluids that formed the carbonate listwaenites were characterized by the presence of $CO_2$, $H_2O$, Ca with only minor $SiO_2$, high pH and moderate temperature (< 300 $^0$C). All of the base and precious metals in both types of listwaenites were extracted from adjoining serpentinite.

## CONCLUSIONS

The silica-carbonate (type I) listwaenite is characterized by presence of quartz+calcite+dolomite +ankerite±magnesite as major rock forming minerals. Carbonate (type II) listwaenite is mainly composed of calcite+dolomite+ankerite with only trace amounts of quartz and magnesite.

Both types of listwaenite have been recognized in the Güvenç and Karakuz areas, whereas only silica-carbonate is seen at Cürek. Silica-carbonate and carbonate listwaenite in

Karakuz were formed along thrust fault zones in or bordering serpentinite. Silica-carbonate listwaenite and some of the carbonate listwaenite in Güvenç were also formed along thrust fault zones; however, most of the carbonate listwaenite was not formed along thrusts. The majority of listwaenites in the Cürek area did not form along faults but were controlled by some small fractures and other secondary permeability features within the serpentines.

Concentrations of $Fe_2O_3$ are greater in silica-carbonate than in carbonate listwaenite (Uçurum, 1996) and base and precious metals-elements are much more enriched in silica-carbonate than they are in carbonate listwaenites. Neither Au or Ag were especially enriched in most of the listwaenites in the study areas, although some local Au and Ag anomalies in the Güvenç and Karakuz area have been detected (Uçurum, 1996). Concentrations of Au and Ag are slightly higher in the silica-carbonate than in carbonate listwaenite.

Listwaenite was formed from serpentinized ultramafic rocks in the Divriği and Kuluncak ophiolitic melanges by hydrothermal fluids in the late Cretaceous. These silica-carbonate listwaenite bodies were formed from a hydrothermal fluid enriched in $SiO_2$, $CO_2$, $H_2O$ and Ca, along thrust fault zones and within a highly serpentinized porous ultramafic zone. The hydrothermal fluids that formed the carbonate listwaenite are characterized by the presence of $CO_2$, $H_2O$, and Ca with only minor $SiO_2$. Base and precious metals in both listwaenite types were extracted in part from adjoining serpentinite. The formation temperature of the listwaenites was between 150 $^0$C and 300 $^0$C.

The formation model submitted here for listwaenite occurrences in east central Anatolia is probably adaptable model for all listwaenite formation in ophiolite belts of Turkey.

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