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[Sobhi Nasir](#)*, [Kamal Noori Khankahdani](#), [Abdel Rahman Nasir](#)

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Article

Hydrothermal Carbonation and Silicification of Harzburgites and Serpentinites in Ophiolites: Geochemical and Petrological Comparison of Listwaenites from Oman and Iran

Sobhi Nasir ^{1,*}, Kamal Noori Khankahdani ² and Abdel Rahman Nasir ³

¹ Earth Sciences Research Centre and UNESCO Chair for Ophiolite Studies, Sultan Qaboos University, Muscat- Oman

² Department of Geology, Shiraz Branch, Islamic Azad University, Shiraz, Islamic Republic of Iran; noorikamal@yahoo.com

³ Western Ontario University, London-Ontario, Canada; Anasir24@uwo.ca

* Correspondence: sobhi@squ.edu.om

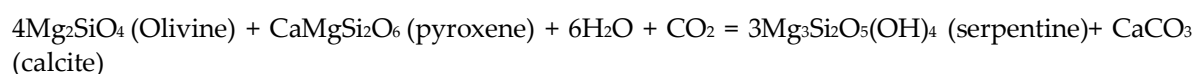
Abstract: Listwaenite rocks are widely spread in Fenja area of the Semail ophiolite of Oman and in Islam Abad area of the Neyriz ophiolite of Iran. There are three types of listwaenites found in these regions: silica-, carbonate-, and carbonate-silica (which includes dolomite, calcite, and magnesite). The alteration of host harzburgites started with hydrothermal alteration to serpentinite, followed by carbonation and silicification of serpentinite. Calcite- and magnesite-dolomite- listwaenites are more abundant in the Fenja area of Oman, while dolomite-listwaenites are more abundant in Islam Abad area in Iran. The mineralogy of listwaenites varies in both Iran and Oman; common minerals include quartz, calcite, goethite, magnesite, dolomite, serpentine, hematite, magnetite, Cr-mica, and Cr-spinel. The major element chemistry of the different types of listwaenites in both Fenja and Islam Abad area generally comparable, and is largely similar to that of hydrothermally carbonated harzburgites, serpentinite, and listwaenites worldwide, despite spanning extraordinary and highly variable contents in major oxides, such as CaO, SiO₂, MgO and LOI. Relict texture and common occurrence of Cr-spinel as well as the high concentrations of Cr, Ni and Co suggest that the protolith of the listwaenites in both regions was serpentinitized harzburgites and serpentinites. In comparison to the primary mantle and chondrite in spider diagrams, the Neyriz listwaenites have higher trace and REE element abundances than comparable listwaenites in the Fenja region. Harzburgite-normalized patterns of trace elements and REE in serpentinite and listwaenites overlap the average composition of harzburgite. PM-normalized trace element and REE patterns for serpentinitized harzburgite and serpentinite show enrichment in Cs, U, Pb and Sr, with no Eu anomaly, comparable to mantle wedge serpentinites. The variable and high abundances of Ca, Mg, Ba, Zr, Sr, Pb, Zn, Mo and W in the carbonate- and silica-carbonate listwaenites, with unique Si enrichment and Mg, Na₂O, Zr, Y, Ba, Sr, Rb, Cu, Pb, Sc, Cs, Nb, Mo and W. depletion in silica listwaenites are indicative of large fluctuations in major and trace element mobility. Cr, Ni and Co were immobile during alteration. Enrichment in Ca and Si could occur by internal or late outside supply. Ca, Mg and Si are conceivably the foremost mobile major components amid harzburgite and serpentinite carbonation with mobilization confirmed by formation of quartz and Mg-carbonate in silica-carbonate listwaenites and quartz in silica listwaenites. The listwaenites in Islam Abad and Fenja area were formed due to hydrothermal alteration of serpentinite along thrust faults and shear zones which acted as pathway for Ca and/or Si rich fluids. The intensity of deformation in Islamabad listwaenites has been higher than Fenja listwaenites as indicated by higher abundance of trace elements.

Keywords: Iran; Oman; Neyriz; Fenja; ophiolite; serpentinite; harzburgites; listwaenites; geochemistry; alteration; hydrothermal

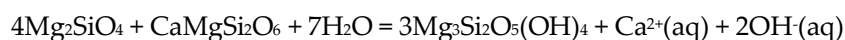
1. Introduction

First time, the term listwaenites (known also as listvenites) was used by Rose [1] to describe gold-bearing carbonate-silicate metasomatic rocks which outcrop in the Listvenya, Ural region. In general, rocks that have undergone alteration processes such as carbonation, silicification, pyritization, and serpentinization of ultramafic rocks are referred to be listwaenites [2,3]. Listwaenites are associated with the majority of ophiolite massifs worldwide, and mainly occur along thrust fault and discontinuities that act as conduits for metasomatic fluids rich in CO₂, Ca and Si [2–14].

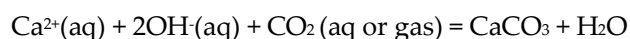
In ultramafic rocks, mantle olivine and pyroxene are unstable near the surface and change to Listwaenites in the presence of CO₂-rich fluids in the temperature range of 80 to 400 °C e.g., [15,16]. However, Falk and Kelemen [17] estimated the temperature formation of Oman's listwaenites at 80 to 130°C. The majority of earlier research indicates that many alteration stages along tectonic contact zones are typically linked to the transformation of ultramafic rocks from ophiolites to listwaenites. A second stage of metasomatic overprinting of serpentinites by carbonate and silica occurs after the first stage of metasomatic serpentinization of ultramafic rocks [2,17–19]. Solid carbonate and silica are the end products of mineral reactions with CO₂ and water. The product of mineral reactions with CO₂ and water are solid carbonate and silica by the following reactions:



This reaction often takes place in stages, e.g.,



in the subsurface, and then the reaction;



depending on the pressure and temperature circumstances under which the reaction occurs, CO₂ (g) represents CO₂ in either gas or supercritical fluid form [20–22].

The Semail ophiolite in Oman and the Neyriz ophiolite in Iran are remnants of the Tethyan oceanic lithosphere obducted tectonically on Oman and Iran toward the end of the Cretaceous, e [23–26]. Listwaenites from various regions of the Semail ophiolite in Oman have been the subject of numerous research [2,17,27–28]. Several studies proposed that the Listwaenite of Oman is a product of post-obductional extension e.g., [2,19], while Falk and Kelemen, [17] proposed that listwaenite was formed during Late Cretaceous ophiolite obduction and ophiolite emplacement in the mantle wedge (95–75 Ma).

Neyriz, Kermanshah, Kurdistan, and Azerbaijani are the four regions where the Zagros ophiolite of Iran outcrops [26,29]. An important area for studying listwaenites and comprehending their geochemical properties in various geological contexts is the Islam Abad area which is primarily linked to the Neyriz ophiolites in Iran. In contrast to those in Oman, where considerable Listwaenites are mostly found in the Fenja region, the listwaenites in these ophiolites in Iran have not been as thoroughly explored e.g., [25,26].

Listwaenite rocks can provide insight into processes of carbon fluxes at the “leading edge of the mantle wedge” in subduction zones and enhanced mineral carbonation of peridotite. The prevalence of listwaenites in Oman and Iran underscores the geological complexity of these regions, offering valuable insights into their tectonic history. This paper aims to provide a comprehensive overview of the geochemistry and petrography of listwaenites in the two prominent regions of Fenja area in Oman and Islam Abad area in Iran. These areas are known for their extensive ophiolite complexes, which host listwaenites occurrences.

2. Methodology

100. samples were collected from the outcropping listwaenites and associated harzburgite and serpentinite in both Fanja area in Oman and Islam Abad in Iran. A representative set of 12 Listwaenite samples with different degrees of deformation were selected for analysis from Islam Abad area in Iran, 13 Listwaenite samples, 4 serpentinitized harzburgite and 4 serpentinite samples were selected from the Fanja area in Oman. Cleaned rock chips from homogeneous sample parts were crushed in an agate mill after washing in distilled water and drying, excluding weathered rims and thicker veins. Major and trace element analysis were carried out using X-Ray fluorescence spectrometry (XRF) and ICP-OES at the ALS Albirq commercial Laboratories in Saudi Arabia. Sample powders were dissolved in a HCl-HNO₃-HF mixture and then analyzed for major and trace elements with an Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) then evaporated to dryness. The cycle of acid and drying was repeated 3 or 4 times. HClO₄ was added during the evaporation stage to insure dissolution. Millipore-filtered distilled water was then added and spiked with 100 ppm Ag and Ta. Three aliquots of the spiked solution were analyzed using the ICP-OES. Multi-element USGS standard were used to calibrate the ICP-OES. Precision for major and minor elements content is estimated to be in the order of 2-5% for major elements and 5 % deviation from true values for trace elements. Analysis quality control and detection limits are given in Supplementary File S-1.

3. Field Description and Geological Setting

3.1. Fanja Area-Oman

Listwaenites in Fanja area are often found within the mantle harzburgites and serpentinites unites, mainly within the basal thrust of the ophiolite section above the underlying metamorphic sole. The majority of listwaenites are found along the frontal range fault and along the Wadi Mansah extensional faults (Figure 1). The listwaenites occur as a suite of WNW and NW- striking bodies that vary in thickness from 1 to 80 m and length from a few kilometers. The outcrops are more resistant to weathering than the harzburgite and serpentinite host rocks because of their yellow to dark reddish brown-, grey-, and orange-colored ridges (Figure 2a). Listwaenite gradually transforms into serpentinite and serpentinitized harzburgite in the field (Figure 2b). Locally, the degree of alteration varies from slight stockwork and quartz-carbonate veining to substantially replaced carbonated and silicified rocks. Near the interface with the serpentinitized harzburgites and serpentinites, the listwaenites are typically veined, brecciated, and severely broken. At the borders between the clast and matrix, individual clasts exhibit signs of repeated brecciation and recementation, such as the termination of clast-hosted veins. Upper mantle rocks in the area comprised of varying serpentinitized harzburgite, serpentinite, pyroxenite dykes, subordinate dunite lenses. In the least serpentinitized areas, common olivine remnants and extremely uncommon primary pyroxene are maintained. Serpentinization is often moderate to intense (80–90%). In most of the serpentinite samples under study, lizardite and chrysotile predominate as serpentine minerals.

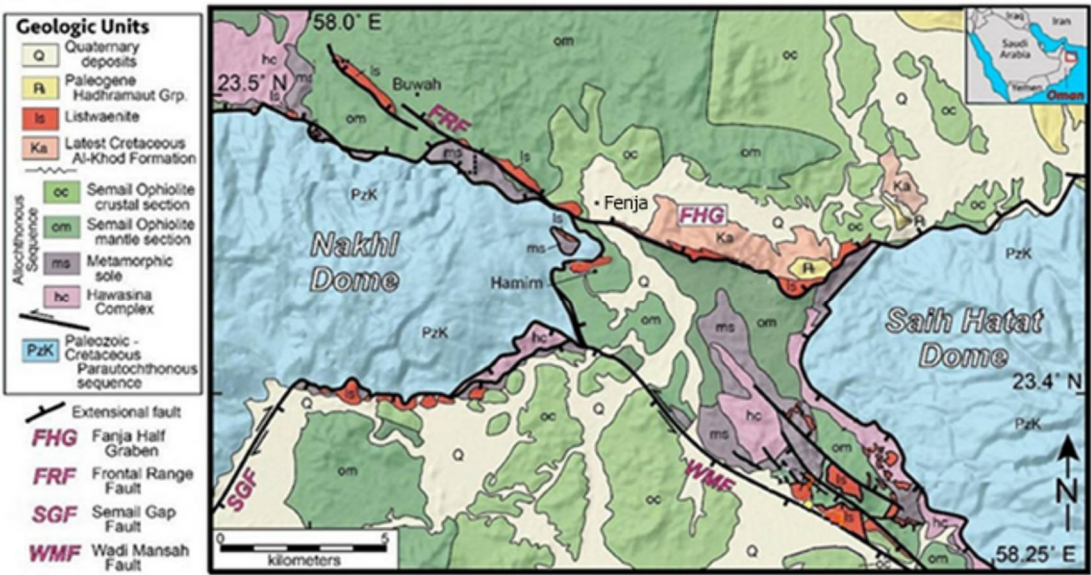


Figure 1. Geological map showing the location of major outcrops of listwaenites in Fenja area modified after [19,30].

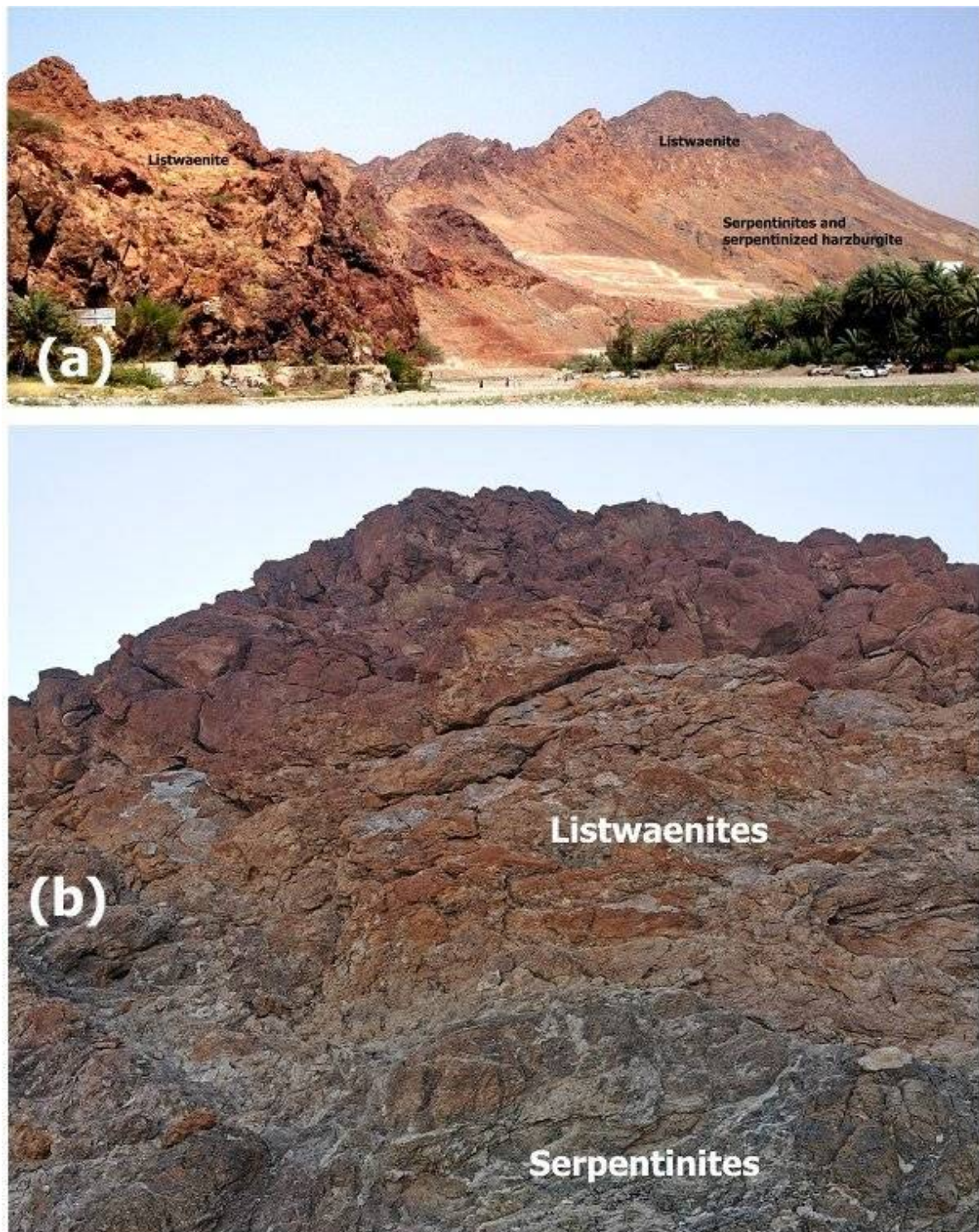


Figure 2. Field photo showing an example of listwaenites ridge in Fenja area (a) and contact between listwaenites and serpentinites (b).

3.2. Islam Abad- Iran

The Listwaenite is located near Islam Abad area, within the Neyriz ophiolite of Iran, close to Islam Abad city (Figure 3). In this region, listwaenites are frequently found in conjunction with serpentinite and harzburgite that has undergone serpentinization. The Neyriz ophiolites in the region comprised of deep sea sedimentary strata (radiolarian cherts) and the entire suite of ultramafic rocks (harzburgite, dunite, and pyroxenite) [31,32]. According to Monsef et al. [33], the Neyriz ophiolite is geotectonically a component of the Iranian Zagros suture zone, which is the most deformed sector of

the continuous collision between the Iranian and Arabian continents. Listwaenites are of variable-size, with erosion-resistant morphological peaks that primarily take the form of abrupt, sheet-like bodies that are 1-2 km broad and 5-20 m thick. The contact between carbonated serpentinite and the neighboring serpentinite occurs as a zone of increasing transition (Figures. 4a to c). A thin layer of harzburgite-rich alteration resembling gossan is present in the majority of instances. There are numerous secondary carbonate minerals (dolomite, magnesite, and calcite) and quartz veinlets in listwaenite rocks, which are fine-to- coarse- and macroscopically heterogeneous with frequent color transitions from dark red to orange, yellow greenish grey to pale grey on a centimeter to meter scale. Along the boundary between serpentines and listwaenites, stockwork structure is widespread, providing evidence for fluid passage and alteration activities (Figure 4c). According to field investigations, Islam Abad listwaenites are connected to thrust fault system zones (Figure 3). Three faults (IF1, IF2, IF3) have been found north of Islam Abad. Apart from sporadic little patches that are still evident inside the serpentinite bodies, ultramafic lithologies that outcrop near listwaenites have nearly entirely changed into serpentinite, as the transformation of the primary minerals into mineral assemblages characterized by opaque mineral phases and serpentine mineral groups is the result of the serpentinization of the ultramafic host rocks. Within serpentinite, many veins of calcite, dolomite, and serpentine intertwine to create a box-like structure.

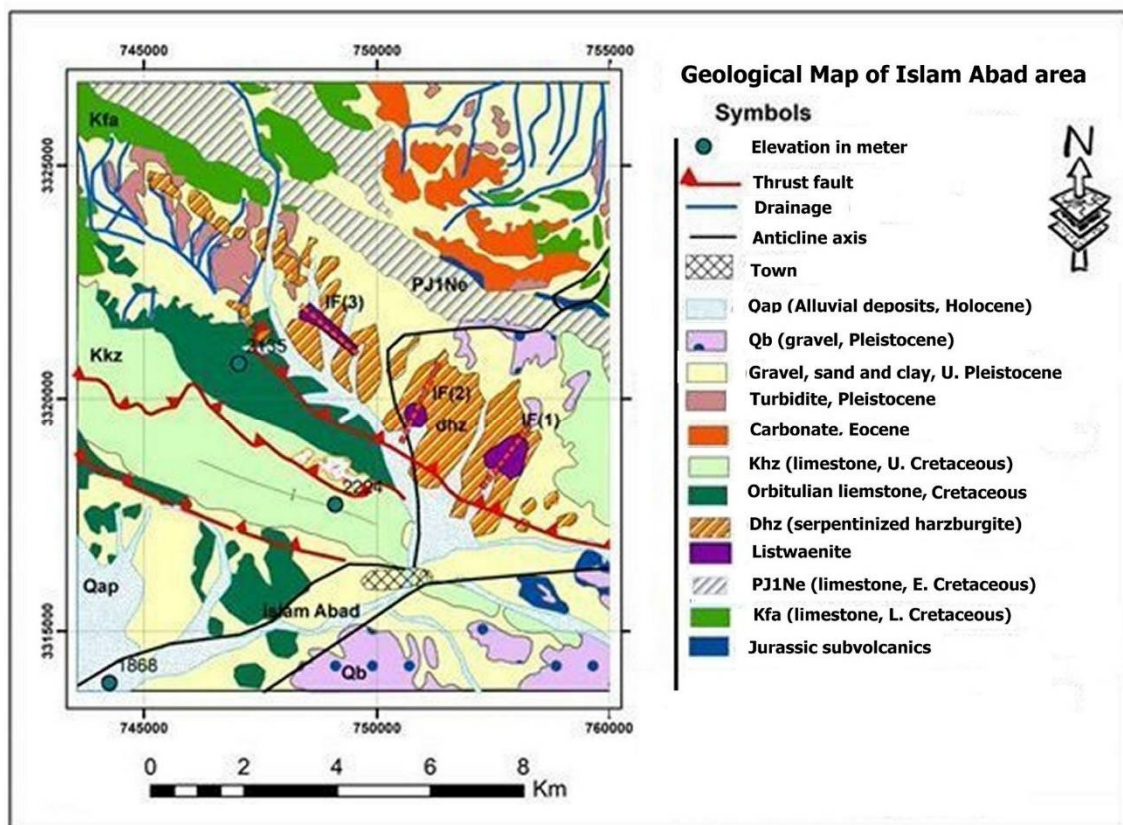


Figure 3. Geological map of Neyriz ophiolite in Islam Abad area Modified after [34–36].

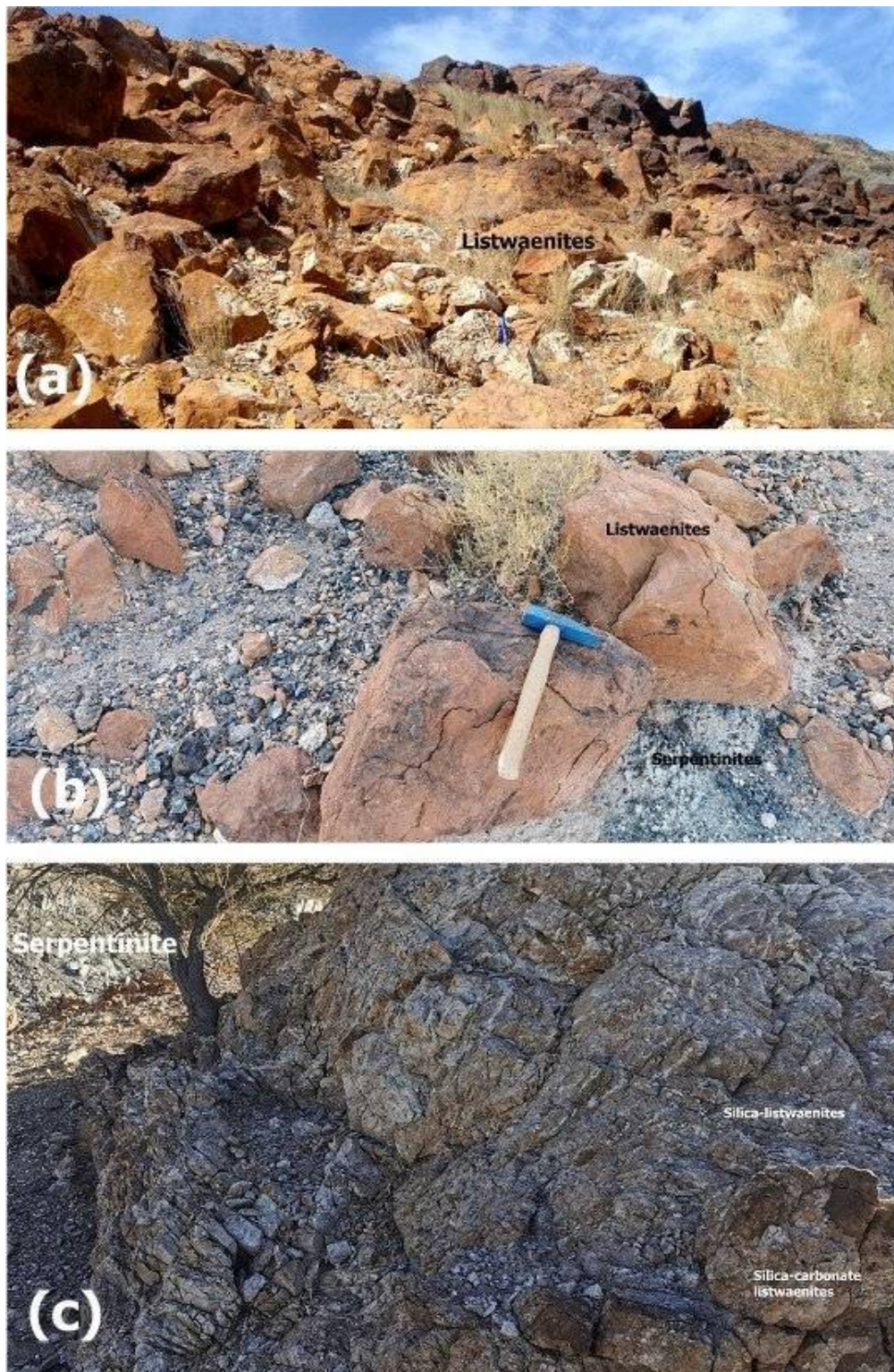


Figure 4. Field photos showing orange brown calcite listwaenites (a), contact between listwaenites and serpentinite (b) and silica- and (c) silica-carbonate listwaenites from Islam Abad area.

4. Petrography

Listwaenites in Islam Abad and Fanja area show variable mineralogy with minerals commonly present include calcite, dolomite, magnesite, quartz, Cr-mica, serpentine, hematite, goethite, magnetite, and Cr-spinel. The results of optical microscopy led to distinguishing three types of listwaenites in both Fanja and Islam Abad areas, namely: silica-listwaenites, silica-carbonate-listwaenites and carbonate-listwaenites (Figures.5 and 6), which are similar to listwaenites types occurring in other ophiolites worldwide [2–11].



Figure 5. Photos of rock samples from Fenja area. (a) Carbonate Listwaenite, (b) Silica-carbonate Listwaenite with white veins and clasts of silica, (c) Silica rich listwaenites.



Figure 6. Photos of rock samples from Islam Abad area. (a) Carbonate Listwaenite, (b) Silica-carbonate Listwaenite with white veins and clasts of silica, (c) Silica rich listwaenites.

4.1. Carbonate Listwaenites

In the Fenja area in Oman, carbonate listwaenites are the most common types of listwaenites. Calcite, a small amount of quartz, goethite and hematite, serpentine, tiny chromite grains, and a few flakes of fuchsite make up the majority of this listwaenites. There are also a few veinlets of colloform magnesite and dolomite. Dolomite typically occurs in aggregate form and has textures ranging from unihedral to subhedral grains. Within the matrix, hematite is the alteration result of magnetite. Sometimes the oxide string distribution in listwaenites is similar to the distribution usually found in serpentine mesh (or hourglass) texture (Figure 7a-b). The predominant minerals found in the transition zone between serpentinites and carbonate listwaenites include dolomite, lizardite, chrysotile, and a minor quantity of brown Cr-spinel. Several samples of this Listwaenite exhibit both macro- and micro- sized voids, with diameters ranging from a few microns to 60 μm . These cavities in the carbonate listwaenites give strong textural evidence for the alteration of less capable minerals that follows percolating fluids and early alteration-dissolution. The carbonate listwaenite from Islam Abad show coarse-grained calcite and several micro veins filled with iron hydroxides and relict Cr-spinel (Figure 7c-d). The skeletal shape of brown Cr-spinel is unihedral to subhedral.

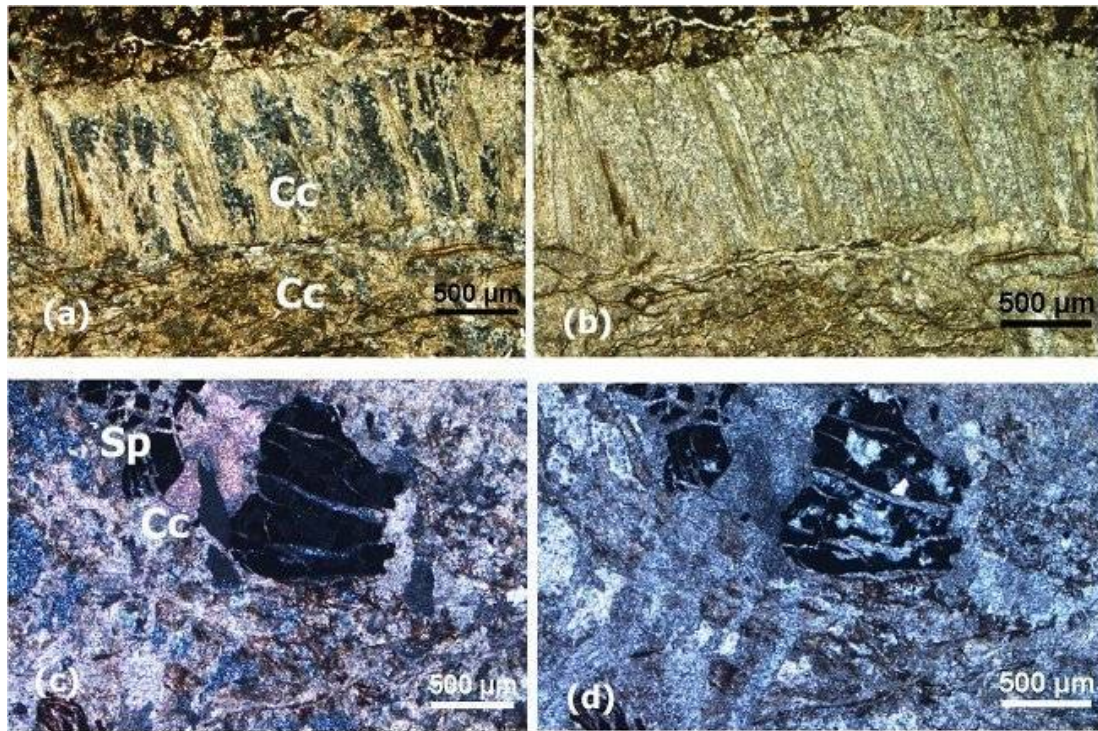


Figure 7. Microscopic images of carbonate listwaenites from Fenja area showing fin grained calcite matrix with micro veins filled with iron hydroxides and wide veins filled with calcite (Cc) replacing serpentinite mesh (a-xpl and b-ppl). Macroscopic images of carbonate listwaenites from Islam Abad area (a-xpl and b-ppl) showing relict of Cr-spinel (Sp) and several micro-veins filled with secondary iron hydroxides and small patches of serpentinite relicts.

4.2. The Silica-Carbonate

In comparison to the other two listwaenites types, the silica-carbonate Listwaenite is less common. It is made up of dolomite, magnesite, calcite, traces of K-bearing minerals (fuchsite), quartz, and remnants of chrome spinel (Figure 8a-b). The pseudomorphic mesh texture found in the protolith of harzburgite is still present. Samples from Fenja area consists mainly of fine to medium grained magnesite, Cr-spinel and several veins filled by quartz. The listwaenites exhibit a gradual carbonate replacement of the remaining serpentine. In comparison, the Listwaenites from Islam Abad consists mainly of coarse-grained dolomite, magnesite and quartz. Dolomite occurs as euhedral rhombic grains replacing serpentine minerals (Figure 8c-d). Quartz grains usually replace dolomite rhombs.

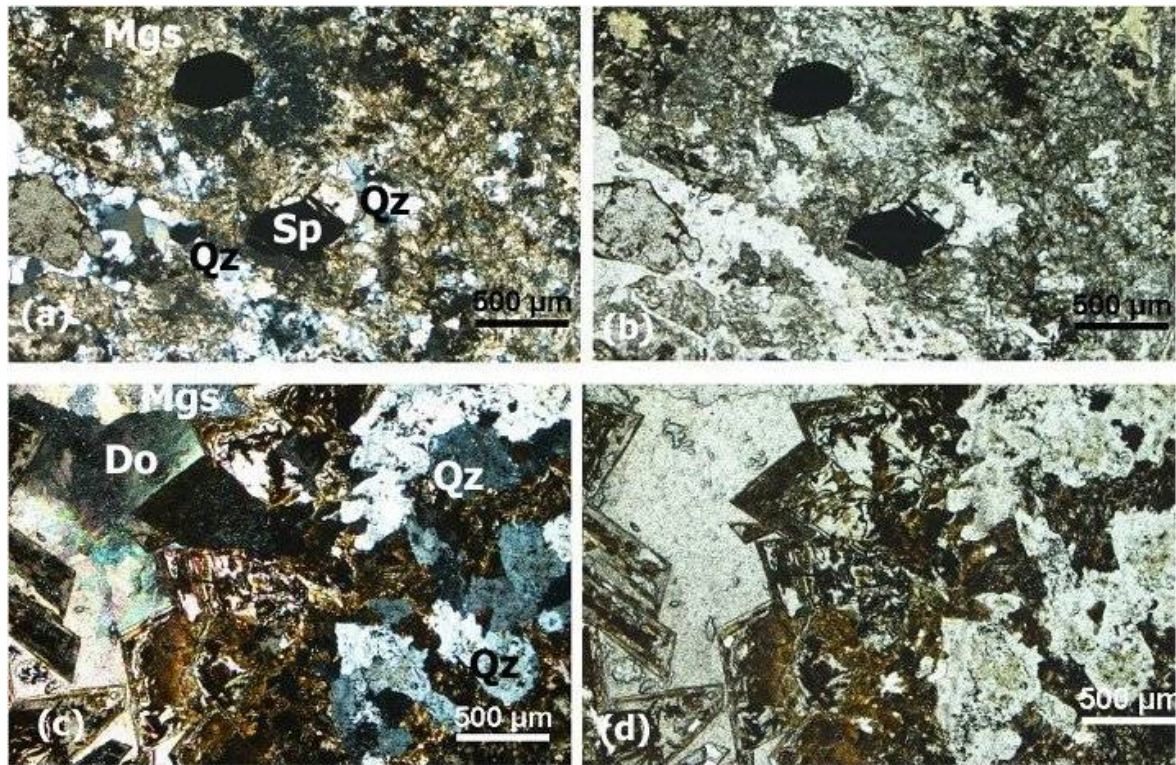


Figure 8. Microscopic images of silica-carbonate listwaenites from Fenja area showing fin grained matrix of magnesite (Mgs) and late stage quartz (Qz) filling veins and relict spinel (Sp) (a-xpl and b-ppl). Microscopic images of silica-carbonate listwaenites from Islam Abad area showing coarse-grained rhombic dolomite (Do), magnesite (Mgs) and later stage quartz replacing carbonate minerals.

4.3. Silica-Listvenites

This Listwaenite is found usually close to the transition zones between the Listwaenite bodies and the neighboring serpentinites. The Listwaenite from both Fenaj and Islam Abad shows similar petrographic features (Figure 9 a-d). It is mainly formed of quartz occurring in two generations. The first generation is primarily made up of opal, chalcedony, cryptocrystalline quartz, serpentine, and remnants of magnetite and chrome spinels. The second generation of silica Listwaenite crosses over into the first generation and is nearly entirely devoid of oxide minerals. It features polycrystalline mosaic, columnar impingement, and comb textures. Quartz occurs as a groundmass that is crosscut polycrystalline and or amorphous quartz veins. The silica Listwaenite are usually brecciated and are porous. Most likely, the porosity indicates carbonate dissolution around the rims of the mesh.

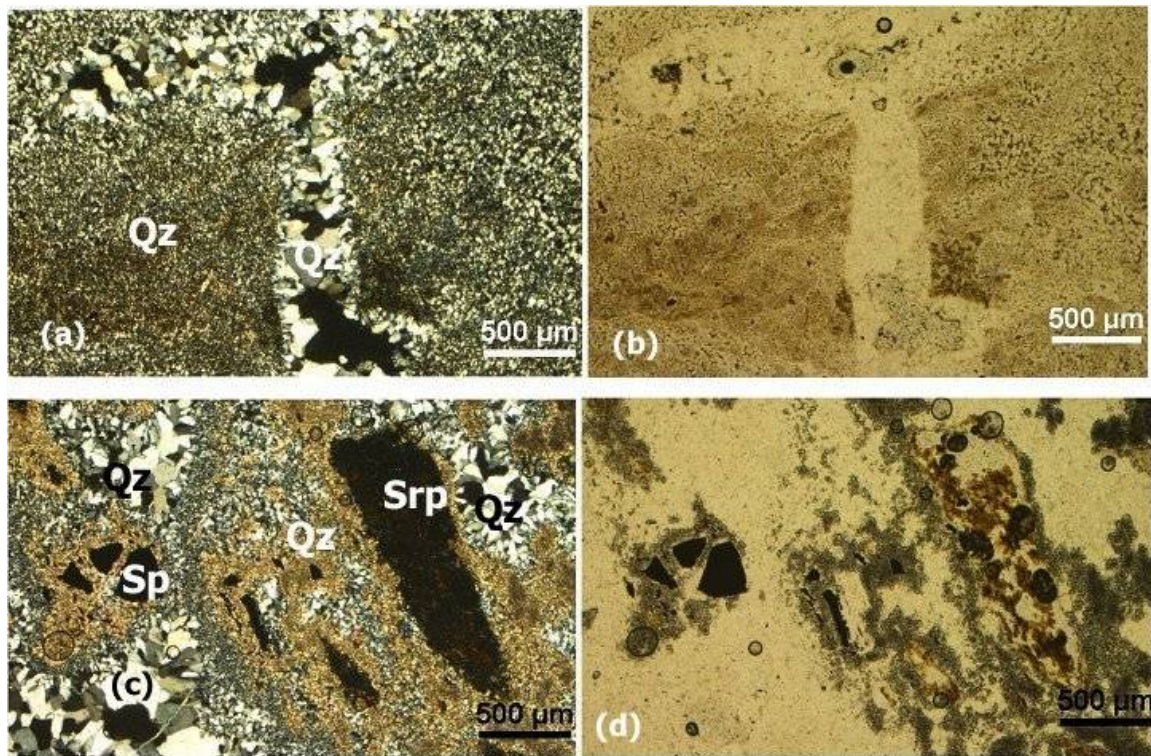


Figure 9. Microscopic images of silica-listwaenites from Fenja area . (a-xpl and b-ppl) showing early stage fine grained quartz matrix and later stage of coarse grained quartz (Qz) filling veins, filled with iron hydroxides and wide veins filled with calcite replacing serpentine mesh. Microscopic images of silica- listwaenites from Islam Abad area (c-xpl and d-ppl) showing fine grained early stage quartz replacing relict serpentine (Srp) and Cr-spinel (Sp) and later stage coarse-grained quartz.

4.4. Serpentinized Harzburgites and Serpentinities

Serpentinized harzburgites are medium- to coarse-grained and are variably serpentinized (~30-40 vol%). Crystals of olivine that have been transformed into lizardite and chrysotile are globular to spherical when broken (Figure 10-a-b). Serpentine exhibits mesh texture and mostly replace olivine and pyroxene in fractures and along cleavage lines (Figure 10 c-d). Most serpentines are chrysotile and lizardite. There are isolated grains of chromite and Cr-spinel that are brecciating and, in certain places, have serpentine veins running through them. Mostly, hematite forms as tiny grains inside of fractures. In heavily serpentinized domains, magnetite typically develops along serpentine veins or on mesh rims. Kink band texture, a sign of tectonic stress, can be seen in certain serpentine minerals in these rocks. Little stages of chromite are seen, containing massive euhedral to anhedral crystals. A small amount of carbonate can be found in the serpentine matrix as spheroidal grains and veins filling. Often, carbonate veins converge with or diverge into preceding serpentine veins.

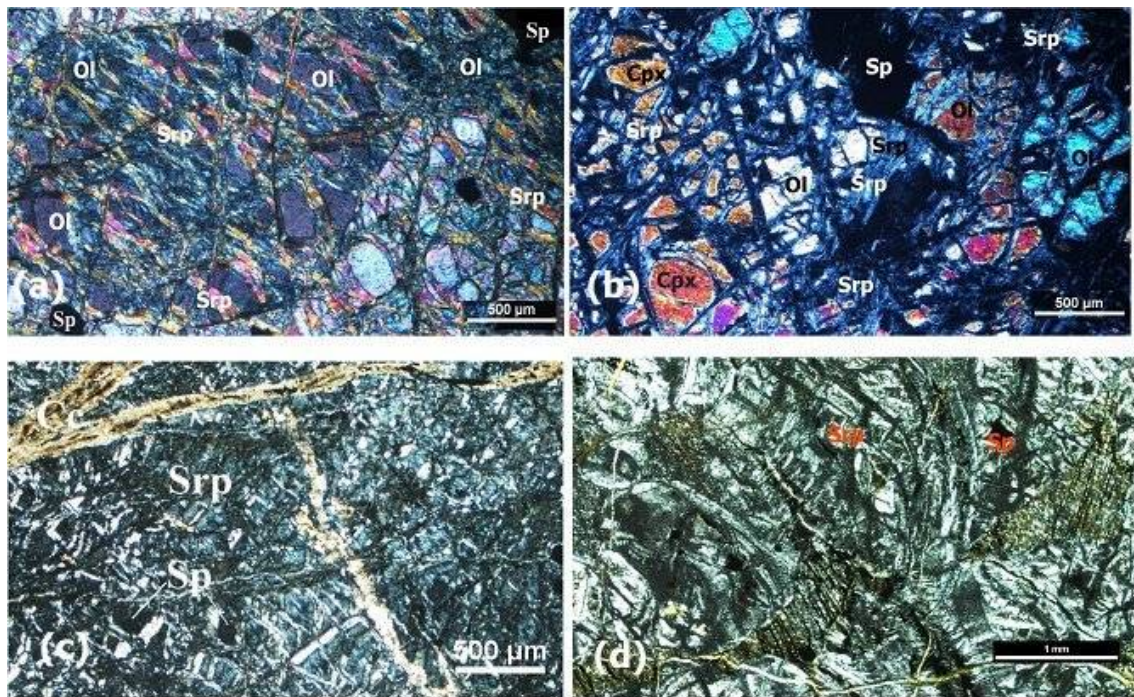


Figure 10. Microscopic images of serpentinitized harzburgite from Fenja area and (a) and Islam Abad (b) showing medium-grained olivine (Ol) altered to serpentine (Srp) and scattered spinel grains (Sp). 10c-d macroscopic images of serpentinites from Fenja (c) and Islam Abad area (d) showing alteration of olivine to serpentine (Srp) and calcite (Cc) filling veins cutting serpentine minerals.

5. Geochemistry

Table 1 presents the chemical analyses of serpentinitized harzburgite, serpentinite, and listwaenites from Fenaj ophiolite in Oman. Table 2. Shows the chemical analysis of listwaenites from Islam Abad area-Neyriz ophiolite in Iran. The averages of different types of listwaenites from Fenja and from Wadi Mansah in Oman [17] and the average of listwaenites, harzburgites and serpentinite from Birjand ophiolite in eastern Iran [26]) and Islam Abad area are also provided for comparison in supplementary file S-2.

Tables 1-2 and major oxide and trace elements variation diagrams (Figure 11a-f and supplementary file S-3) show that the different types of listwaenites from both Iran and Oman have variable major and trace element composition. All listwaenite types in both Oman and Iran have low Al_2O_3 (<1.2 wt.%), K_2O (<0.14 wt.%), Na_2O (<0.12 wt. %) and TiO_2 content (<0.04) (Figure 11), as well as low high field strength elements incompatible lithophile trace elements and REE. K_2O is higher in the silica-carbonate from Iran compared to those in the silica-carbonate listwaenites from Oman and other two types of silica- and carbonate- listwaenites. The MnO , Na_2O , TiO_2 and Al_2O_3 contents in most samples overlap and compared to those contents in the associated serpentinites and harzburgites (supplementary file 3). Fe_2O_3 content is high (9.2-11.5 wt. %) in the carbonate and carbonate-silica listwaenites, while it is lower in the silica listwaenites and associated ultramafic rocks (6.6-9.1wt.%). The listwaenites from Oman show higher Fe_2O_3 contents than those from Iran. Silica-carbonate listwaenites plot as a distinct group between the field of silica- and carbonate-listwaenites. The three types of listwaenites are characterized by high Ni (1350-2750 ppm), Cr_2O_3 (0.2-0.45 wt. %) and Co (63-115 ppm). which overlaps the composition of host serpentinitized harzburgites and serpentinites from the study area (Table 1-2, Figure 11f, and supplementary files S-3).

Carbonate- and silica- listwaenites in both Iran and Oman have low MgO (4.5 to 11.5 wt.%), while the carbonate-silica listwaenites from Iran have higher MgO (30.5 to 33.9 wt.%) than those from Oman (21.3 to 23.4 wt.%), but lower than MgO content in the associated serpentinites and harzburgite (35-40 wt.).The $\text{MgO} + \text{CaO}$ wt.% in the carbonate and carbonate-silica listwaenites overlap the content in the associated serpentinites and harzburgites, while it is lower in the silica-listwaenites (Figure 12a-d) The SiO_2 content show a wide range from 3 wt.% in the carbonate listwaenites to 80.6 wt.% in the silica listwaenites. The CaO content also shows a wide range from 1.3

wt.% in the silica listwaenites to 37.5 wt. % in the carbonate listwaenites. Higher LOI in carbonate and silica-carbonate listwaenites together with high MgO content in carbonate-silica listwaenites, is consistent with the presence of magnesite and dolomite as the most abundant carbonate mineral in the carbonate-silica listwaenites, and calcite in the carbonate listwaenites. Figure 12c shows a clear positive relationship between LOI and the three types of studied listwaenites. Serpentinite compositions overlap and compared to serpentinized harzburgite protolith (Table 1, Figure 12a-d). Molar MgO, CaO and Mg# versus molar SiO₂ diagrams show similar variations of these oxides in the analyzed lithologies (Figure 12b, d).

Table 1. Major and trace element analysis of listwaenites from Fenja area-Oman.

Sample	FCL-10	FCL-11	FCL-12	FCL-13	FDL-6	FDL-7	FDL-8	FDL-9	FSL-1	FSL-2	FSL-3	FSL-4	FSL-5
Type	Carbonate-Listwaenite				Silica carbonate listwaenites				Silica listwaenites				
SiO ₂ wt. %	4.4	5.3	6.5	3.8	21.5	17.5	19.7	20.1	71.8	60.13	68.5	69.9	70.8
TiO ₂	0.02	0.01	0.02	0.04	0.03	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.01
Al ₂ O ₃	1.15	1.02	0.95	1.2	0.63	0.6	0.58	0.69	0.15	0.18	0.21	0.38	0.41
Fe ₂ O ₃	11.45	11.2	10.55	11.9	11.28	10.43	11.45	11.11	8.23	9.12	8.5	7.55	8.25
MgO	4.76	7.9	6.45	6.5	21.35	22.9	21.76	23.4	8.45	11.1	7.8	9.14	9.05
MnO	0.16	0.24	0.13	0.11	0.19	0.15	0.13	0.17	0.1	0.11	0.12	0.08	0.09
CaO	37.5	35.14	37.2	36.8	19.3	22.6	23.45	21.85	2.45	4.6	3.1	1.4	2.1
Na ₂ O	0.1	0.1	0.1	0.1	0.11	0.1	0.1	0.1	0.1	0.1	0.1	0.12	0.1
K ₂ O	0.08	0.06	0.05	0.06	0.1	0.1	0.12	0.14	0.02	0.03	0.02	0.03	0.04
P ₂ O ₅	0.01	0.03	0.02	0.01	0.03	0.03	0.01	0.02	0.01	0.01	0.01	0.01	0.01
LOI	39.6	38.3	37.5	38.5	25.4	26.1	22.7	23.1	8.1	14.1	11.2	10.4	8.65
Total	99.23	99.3	99.47	99.02	99.92	100.52	100.01	100.7	99.43	99.5	99.58	99.03	99.51
Mg#	45.17	58.3	54.79	51.98	78.95	81.31	79.02	80.67	67.05	70.69	64.52	70.58	68.5
Sc ppm	4.01	4.32	4.41	4.79	4.66	5.91	5.65	4.22	4.8	4.72	4.35	4.61	4.74
As	3.1	4.1	4.4	5.1	5	7	9	7	24	27	34	37	25
Ba	3.9	3.7	3.4	2.8	3.5	3.9	4.8	5.1	44	37	20	29	18
Co	115	95	120	102	90	92	110	86	71	62	73	65	63
Cu	5.8	4.2	5.8	8.5	3	3	2	2.5	11	14	10	8	9
Zn	275	155	320	345	283	255	315	260	36	55	61	69	72
Ni	2650	2470	2690	2750	2200	2700	2600	2090	1500	1550	1600	1350	1360
Ga	0.75	0.56	0.64	0.75	0.26	0.3	0.25	0.35	0.35	0.25	0.4	0.43	0.35
Cr	3100	2600	3200	3300	2000	2400	2100	1900	1400	1600	1400	1500	1500
V	36	33	35	46	17	18	13	17	14	13	16	15	13
Rb	0.13	0.12	0.19	0.17	0.08	0.059	0.1	0.18	0.03	0.08	0.05	0.06	0.09
Sr	150	225	183	165	145	210	175	195	37	39	42	46	35
Zr	0.06	0.02	0.05	0.02	0.05	0.01	0.01	0.02	0.17	0.17	0.04	0.05	0.03
Sb	0.41	0.37	0.39	0.33	1.15	1.52	2.2	2.7	0.85	1	0.3	0.55	0.64
Cs	0.21	0.15	0.27	0.16	0.14	0.13	0.16	0.17	0.21	0.25	0.18	0.16	0.13
Nb	0.013	0.08	0.07	0.09	0.019	0.016	0.015	0.039	0.006	0.005	0.004	0.003	0.02
Y	0.22	0.17	0.34	0.53	0.04	0.03	0.04	0.15	0.14	0.13	0.09	0.07	0.06
La	0.0201	0.0238	0.0172	0.0195	0.0055	0.0051	0.0045	0.0061	0.0071	0.0128	0.0099	0.0091	0.0065
Ce	0.043	0.049	0.036	0.039	0.015	0.013	0.011	0.018	0.017	0.025	0.02	0.018	0.016
Pr	0.0048	0.0052	0.0041	0.0045	0.0023	0.0021	0.0018	0.0027	0.0037	0.0045	0.0043	0.004	0.0036
Nd	0.026	0.027	0.019	0.024	0.014	0.011	0.01	0.017	0.022	0.028	0.024	0.023	0.017
Sm	0.013	0.014	0.009	0.012	0.008	0.007	0.006	0.01	0.008	0.015	0.011	0.009	0.007
Eu	0.0059	0.0061	0.0047	0.0057	0.006	0.0055	0.0051	0.0065	0.0027	0.007	0.004	0.0035	0.0025
Gd	0.02	0.023	0.015	0.019	0.033	0.028	0.025	0.038	0.01	0.022	0.014	0.013	0.009
Tb	0.0041	0.0045	0.0029	0.0039	0.0075	0.0057	0.0051	0.008	0.002	0.004	0.0024	0.0025	0.0016
Dy	0.026	0.028	0.022	0.024	0.041	0.038	0.035	0.045	0.015	0.025	0.018	0.016	0.011
Ho	0.0056	0.0058	0.0048	0.0054	0.0091	0.0085	0.0081	0.0096	0.003	0.006	0.0035	0.0032	0.0025
Er	0.019	0.022	0.013	0.017	0.033	0.028	0.025	0.035	0.01	0.019	0.013	0.011	0.009

Tm	0.0029	0.0036	0.0024	0.0031	0.0048	0.0044	0.0042	0.0055	0.0015	0.003	0.002	0.0017	0.0013
Yb	0.023	0.024	0.017	0.022	0.031	0.028	0.025	0.035	0.01	0.021	0.012	0.011	0.009
Lu	0.0037	0.0042	0.0025	0.0035	0.0054	0.0051	0.0046	0.0058	0.0015	0.0029	0.002	0.0018	0.0012
Mo	0.13	0.14	0.17	0.12	0.32	0.41	0.37	0.42	0.55	0.38	0.42	0.45	0.51
W	1.1	0.95	1.25	1.34	1.77	1.65	1.85	1.92	2.2	1.98	2.05	2.45	1.87
Pb	19	14.1	11.5	10.3	41	42	35	38	3.1	3.6	4	4.5	4.4
Th	0.14	0.11	0.09	0.08	0.15	0.13	0.14	0.12	0.09	0.11	0.1	0.13	0.08
U	0.06	0.05	0.07	0.07	0.08	0.09	0.12	0.16	0.15	0.17	0.18	0.2	0.16

Table 2. Major and trace element analysis of listwaenites from Islam Abad-Neyriz ophiolite-Iran.

Sample	NCL-1	NCL-2	NCL-3	NCL-4	NDL-9	NDL-10	NDL-11	NDL-12	NSL-5	NSL-6	NSL-7	NSL-8
Type	Carbonate listwaenites				Silica carbonate listwaenites				Silica listwaenites			
SiO2 wt. %	3.12	3.63	4.22	7.19	24.37	23.56	24.74	25.15	76.54	73.44	80.59	77.23
TiO2	0.03	0.024	0.021	0.01	0.01	0.01	0.03	0.02	0.01	0.01	0.02	0.02
Al2O3	0.54	0.52	0.43	0.44	0.38	0.45	0.54	0.32	0.25	0.22	0.15	0.19
Fe2O3	9.2	9.92	10.75	10.17	10.71	11.31	10.61	10.13	6.65	7.87	7.15	7.45
MgO	9.11	9.45	8.9	8.8	30.55	31.09	33.88	30.55	5.27	5.81	4.45	5.11
MnO	0.03	0.05	0.04	0.16	0.1	0.09	0.08	0.05	0.03	0.058	0.12	0.055
CaO	34.14	33.11	32.5	32.78	9.18	11.05	10.66	10.95	4.85	3.09	1.31	4.07
Na2O	0.01	0.01	0.01	0.06	0.07	0.07	0.08	0.06	0.02	0.01	0.01	0.01
K2O	0.03	0.04	0.02	0.01	0.02	0.05	0.09	0.02	0.01	0.02	0.01	0.02
P2O5	0.03	0.05	0.04	0.02	0.01	0.01	0.02	0.02	0.05	0.06	0.08	0.06
LOI	43.36	42.52	43.12	40.95	24.1	22.1	19.15	22.6	6.3	8.12	6.06	5.4
Total	99.6	99.32	100.05	100.59	99.5	99.79	99.88	99.87	99.98	98.71	99.96	99.61
Mg#	66.25	65.37	62.13	63.17	84.97	84.49	86.35	85.67	61.1	59.4	55.23	57.62
Sc ppm	4.61	3.23	4.98	5.05	5.92	5.23	5.11	5.19	5.44	4.87	5.01	4.92
As	3.7	4.9	4.8	4.3	6.1	5.1	5.8	7.6	17.9	15.5	19.2	12.1
Ba	32.94	31.8	33.52	29.94	6.84	7	9.38	13.45	19.94	17.01	21.38	22.6
Co	107	102	93	91	60	54	71	78	78	62	59	66
Cu	2.75	1.2	3.1	6.01	0.42	0.48	0.57	0.55	1.75	1.15	0.92	1.07
Zn		120.3	112.9	81.31	248	322	169	183.5	91.2	242	171	118.2
Ni	2682	2475	2219	2165	991	1092	1540	1890	955	1154	965	1306
Ga	0.7	0.51	0.76	0.59	0.51	0.59	0.48	0.45	1.52	0.95	1.54	1.43
Cr	2945	2808	2433	2205	2710	2212	1998	1885	1690	1750	1610	1350
V	38.2	33.6	41.4	33.5	26.6	24.5	27.8	25.4	24.5	23.6	20.5	19.1
Rb	0.14	0.11	0.09	0.15	1.1	1.7	1.4	1.34	5.12	3.81	6.54	3.78
Sr	249	237	242	278	192	177	138	142	29.1	33.5	36.1	40.6
Zr	0.06	0.03	0.02	0.03	0.178	0.164	0.191	0.254	0.31	0.5	0.44	0.48
Sb	11.2	12.6	10.05	10.82	26.5	24.9	20.89	23.3	8.5	5.3	9.4	6.6
Cs	0.285	0.149	0.153	0.235	0.667	0.703	0.834	1.097	1.812	1.244	2.719	1.162
Nb	0.71	0.31	0.119	0.194	0.41	0.71	0.27	0.6	0.92	0.61	0.41	0.61
Y	0.27	0.18	0.31	0.29	0.35	0.41	0.32	0.29	0.95	0.88	0.73	0.67
La	1.253	1.144	1.441	0.976	0.39	0.34	0.22	0.233	0.124	0.063	0.085	0.153
Ce	2.552	2.241	3.154	2.031	0.551	0.442	0.401	0.42	0.158	0.101	0.114	0.235
Pr	0.271	0.239	0.392	0.206	0.066	0.058	0.049	0.051	0.021	0.011	0.015	0.038
Nd	1.293	1.096	1.651	0.961	0.339	0.312	0.251	0.292	0.098	0.048	0.059	0.157
Sm	0.371	0.294	0.431	0.198	0.127	0.101	0.062	0.095	0.035	0.015	0.019	0.056
Eu	0.101	0.084	0.13	0.069	0.051	0.04	0.026	0.034	0.018	0.006	0.01	0.031
Gd	0.225	0.195	0.331	0.155	0.171	0.133	0.08	0.101	0.064	0.015	0.031	0.087
Tb	0.037	0.026	0.051	0.019	0.046	0.037	0.026	0.031	0.01	0.003	0.006	0.015
Dy	0.215	0.182	0.331	0.151	0.418	0.398	0.261	0.351	0.07	0.021	0.037	0.105
Ho	0.053	0.038	0.074	0.03	0.116	0.101	0.061	0.082	0.014	0.005	0.01	0.029
Er	0.141	0.109	0.191	0.081	0.35	0.301	0.221	0.281	0.041	0.015	0.029	0.091

Tm	0.019	0.015	0.024	0.013	0.055	0.053	0.037	0.045	0.007	0.002	0.005	0.012
Yb	0.105	0.081	0.171	0.074	0.39	0.327	0.207	0.301	0.049	0.017	0.035	0.091
Lu	0.015	0.012	0.023	0.01	0.064	0.053	0.031	0.042	0.009	0.003	0.005	0.016
Mo	0.13	0.12	0.16	0.18	0.33	0.28	0.37	0.32	0.55	0.45	0.42	0.38
W	1.86	1.65	1.56	1.76	1.45	1.38	1.74	1.68	2.82	2.95	2.55	3.58
Pb	40.7	33.8	43.4	37.1	8.6	9.1	7.9	8.1	4.5	3.45	2.78	4.1
Th	0.1	0.17	0.21	0.14	0.16	0.08	0.15	0.2	0.12	0.1	0.09	0.11
U	0.085	0.07	0.065	0.079	0.04	0.06	0.05	0.07	0.13	0.15	0.16	0.14

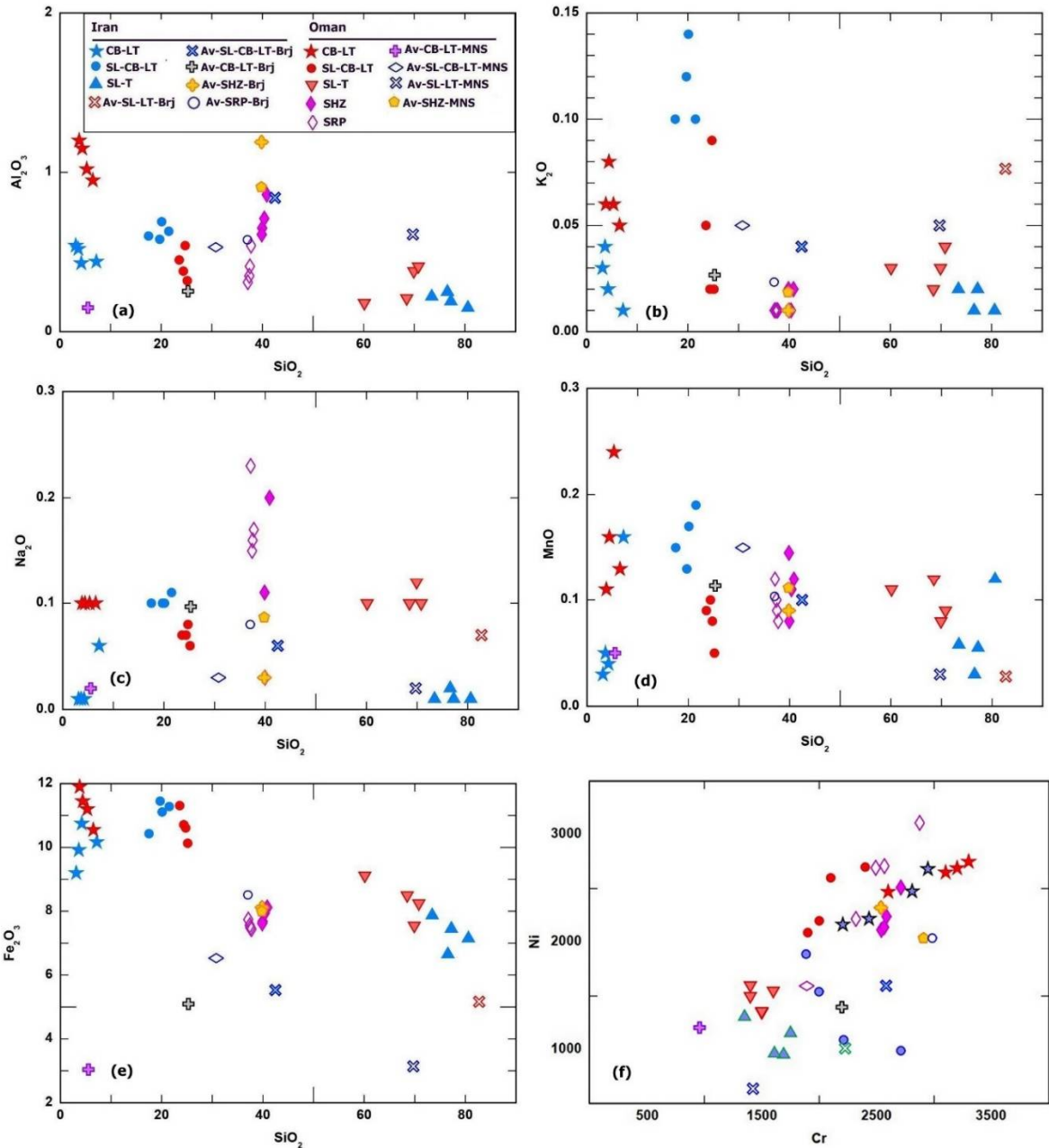


Figure 11. a-f. Binary variation diagrams of SiO₂ vs. selected major oxides (a-e) and Cr vs. Ni (f) in listwaenites, serpentinites and harzburgite from Fenja and Islam Abad.

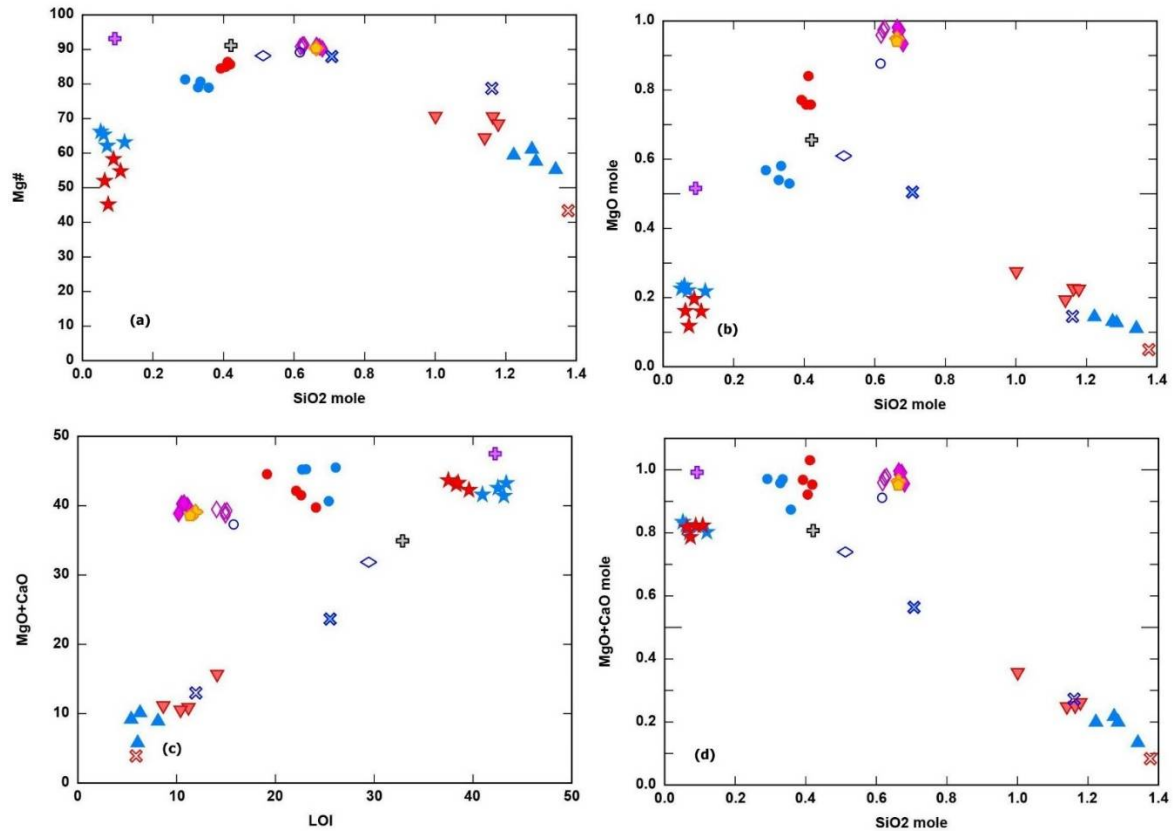


Figure 12. a-d. Binary variation diagrams (a) SiO₂ mole vs. Mg#, (b) SiO₂ mole vs MgO mole, (c) LOI vs. MgO + CaO and (d) SiO₂ mole vs MgO + CaO mole. Symbols as in Figure 11.

Triangular diagrams MgO–CaO–SiO₂ (Figure 13a), SiO₂–Fe₂O₃–CaO + Mg (Figure 13b), MgO + CaO–LOI–SiO₂ (Figure 13a-c) show that the Listwaenite samples can be classified into the three categories described above: silica-, carbonate-, and silica-carbonate listwaenites. Partially serpentinized harzburgites and serpentinites show comparable compositions and plot close to the center of MgO–SiO₂, MgO+CaO–SiO₂ and MgO + CaO–SiO₂–LOI tie lines (Figure 13a-c).

Listwaenites have higher compositional variability, with the three Listwaenite fields mostly governed by changeable MgO + CaO–SiO₂ and LOI, setting them apart from partially serpentinized harzburgites and serpentinites.

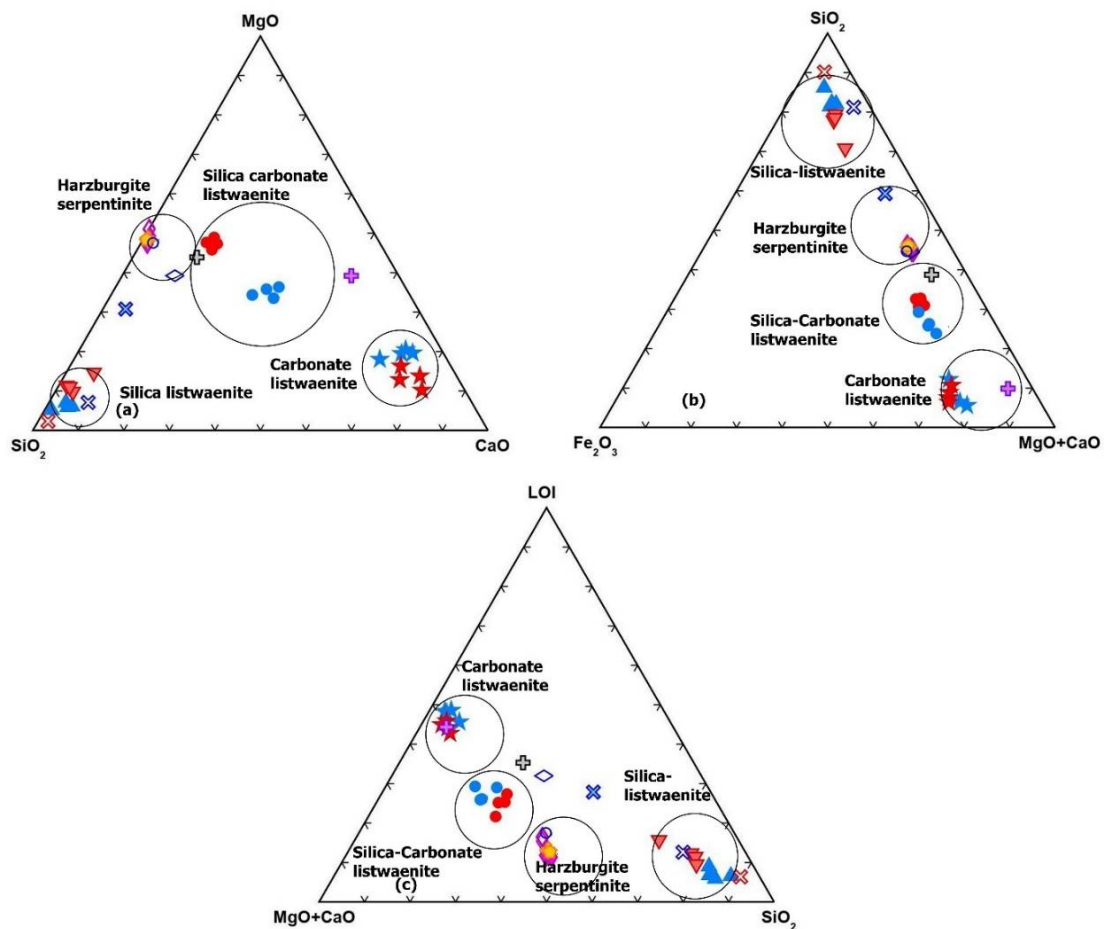


Figure 13. Triangular diagrams. (a) SiO_2 - CaO - MgO , (b) Fe_2O_3 - MgO + CaO - SiO_2 and (c) MgO + CaO - SiO_2 - LOI . Symbols as in Figure 11.

Figure 14a-b display the chondrite-normalized REE patterns for listwaenites, serpentinites, and harzburgites from Oman and Iran. All the examined lithologies have relatively similar rare earth element patterns, showing flat REE patterns that are comparable to those of related serpentinitized harzburgite and serpentinite, which have a spoon pattern with lower LREE (Figure.). The carbonate listwaenites from Birjand ophiolite of Iran show a positive Eu anomaly (Figure 14-c), whereas the serpentinite shows a negative anomaly, while the silica and silica-carbonate listwaenites show similar pattern to those from Oman and Islam Abad ophiolite. The REE contents of Iranian listwaenites are higher than those of Oman. All Listwaenite samples, however, have extremely low concentrations of rare earth elements; for example, the average REE total for listwaenites from Iran and Oman is 2.21 ppm and 1.82 ppm, respectively, while for serpentinites it is 0.26 and 0.27 ppm, and for serpentinitized harzburgite from Iran and Oman it is 0.15 and 0.13 ppm respectively.

Figure 15a-c show-normalized diagrams of REE and trace elements in the studied lithologies. Compared to the harzburgite and serpentinite protolith, listwaenite lithologies from Islam Abad and Birjand ophiolites in Iran and Fanja in Oman show similar pattern but exhibit higher PM-normalized abundances (~ 5 to $900\times$ PM) for Cs, U, K, Pb, and Sr (Figure 15a, b). The trace element contents of Iranian listwaenites are somewhat higher than those of Oman. In partially serpentinitized harzburgite and serpentinites, PM-normalized patterns clearly demonstrate enrichment (~ 5 to $\sim 100\times$ PM) in Cs, Ba, U, Pb, and Sr, whereas other trace element abundances are within or below PM values.

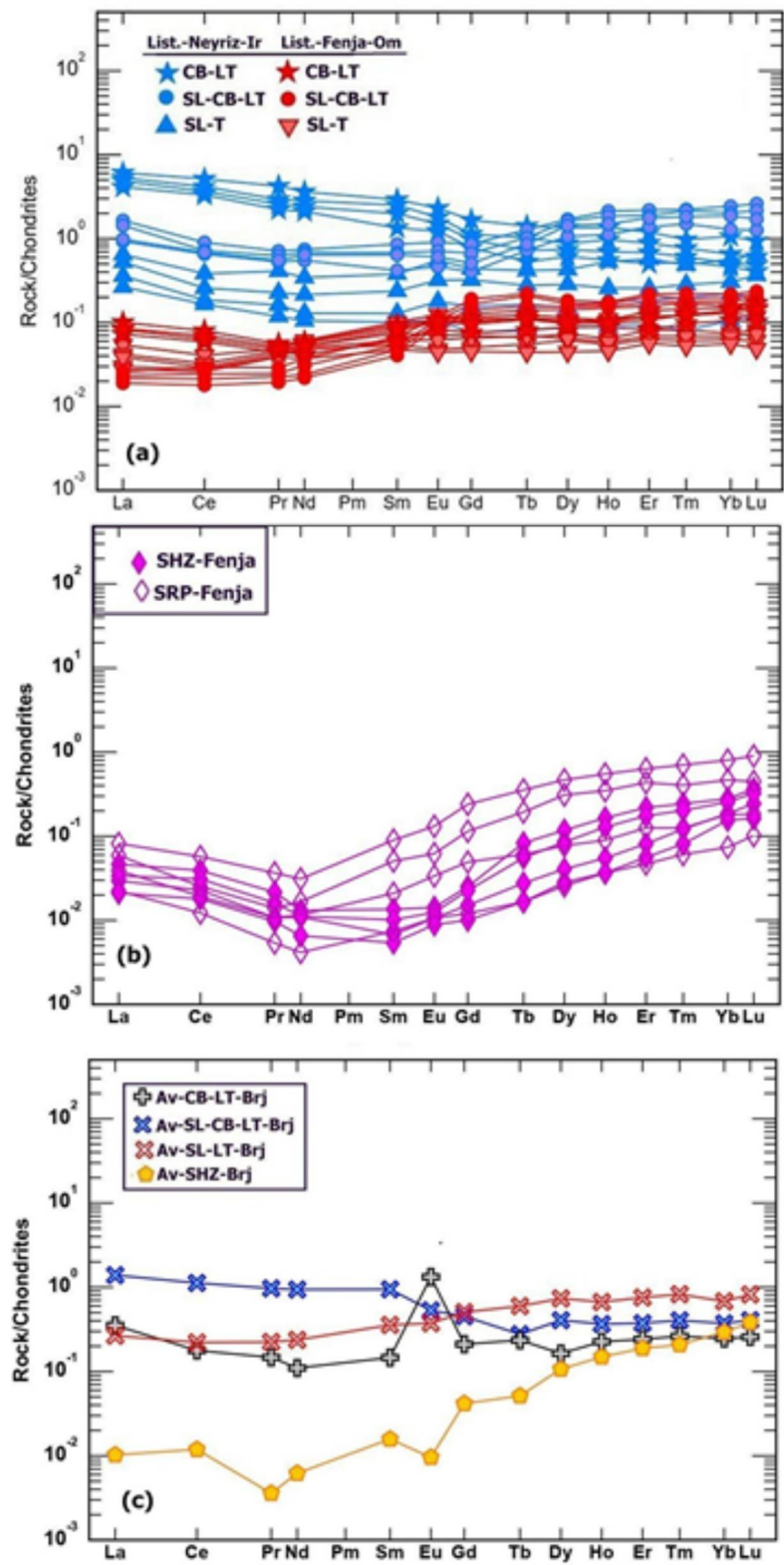


Figure 14. (a) REE normalization diagram after McDonough and Sun [37] of listwaenite lithologies from Fenja and Islam Abad (Neyriz ophiolite) (b) REE pattern of serpentinite and harzburgite from Fenja area, (c) REE pattern of listwaenite and harzburgite from Birjand area (Brj), Iran [26].

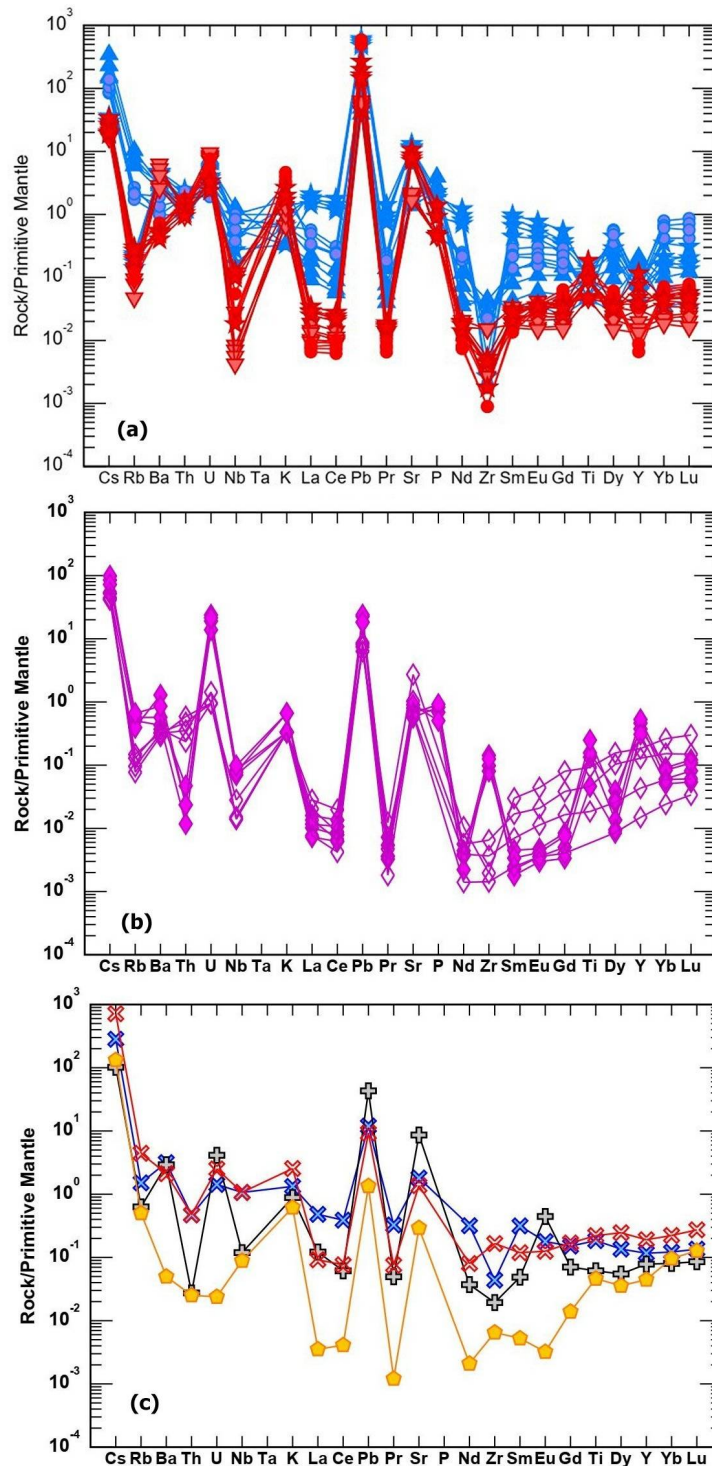


Figure 15. (a) PM-normalized diagrams trace elements after Sun and McDonough [38] in listwaenite lithologies in Fenja and Islam Abad area. (b) and in serpentinite and harzburgite from Fenja area (b) (c) listwaenites in Birjand area in Iran (c) [26]. Symbol as in Figure 14.

6. Discussion

6.1. Element Mobility

The major, trace element, and REE harzburgite-normalized patterns in listwaenites generally correspond to the average harzburgite composition, with the exception of slight to moderate loss in SiO_2 , TiO_2 , Al_2O_3 , MnO , MgO , Cu , V , and Nb , and high gains in CaO , K_2O , Ba , Zr , Sr , Pb , Zn , Mo , and W in the carbonate- and carbonate-silica listwaenites (Figure 16). The levels of Cr , Ni , and Co are comparable to those found in harzburgites (Figure 11f, Table 1). By contrast, the silica listwaenites

exhibit moderate to high losses in MgO, Na₂O, Zr, Y, Ba, Sr, Rb, Cu, Pb, Sc, Cs, Nb, Mo, and W, and low to moderate gains in SiO₂ and CaO. These differences could result from the hydrating fluids' properties or could be inherited from the effects of serpentinization, carbonation, and silicification on the harzburgite protolith's composition, which can cause these elements to be gained or lost before complete alteration. The harzburgite protolith may have interacted with fluids derived from sediment, as suggested by the observed enrichments in Ca and Sr [39–41]. Figure 17a shows that the elements Ti, Al, Fe, Mn, Na, K and P are not deviated or show very slight deviation from the average serpentinite, while Si show high positive deviations in the silica listwaenites (+23 to +34 in Fenja and +36 to +43 in Islam Abad), but negative deviations (-12 to -34) in the carbonate and carbonate-silica-listwaenites. Ca and LOI show high positive deviation in the carbonate listwaenite and moderate positive deviation in the carbonate-silica-listwaenite and slight negative deviation in the silica listwaenites. Figure 17b shows that Cr is more enriched in the Oman listwaenite, while Ni is more enriched in the Iranian listwaenite. Sr and Zn show moderate enrichment in the listwaenites, while other trace elements show only slight deviation from serpentinite.

The low Mg# and MgO depletion in silica listwaenites is most likely due to mobility of Mg as the Fe content of this type of listwaenites is comparable to that of silica-carbonate and carbonate listwaenites (Figure 12). This may indicate release of Mg from carbonate from the silica-carbonate listwaenites and replacement by Si from a later Si-rich fluid with lower pH. Mg mobility is not obvious in the carbonate-silica listwaenites as these elements show relatively similar concentrations to their harzburgite protolith, thus showing low mobility on the harzburgite-normalized patterns. However, Mg, Si and Ca mobility is obvious in the carbonate- and silica-listwaenites.

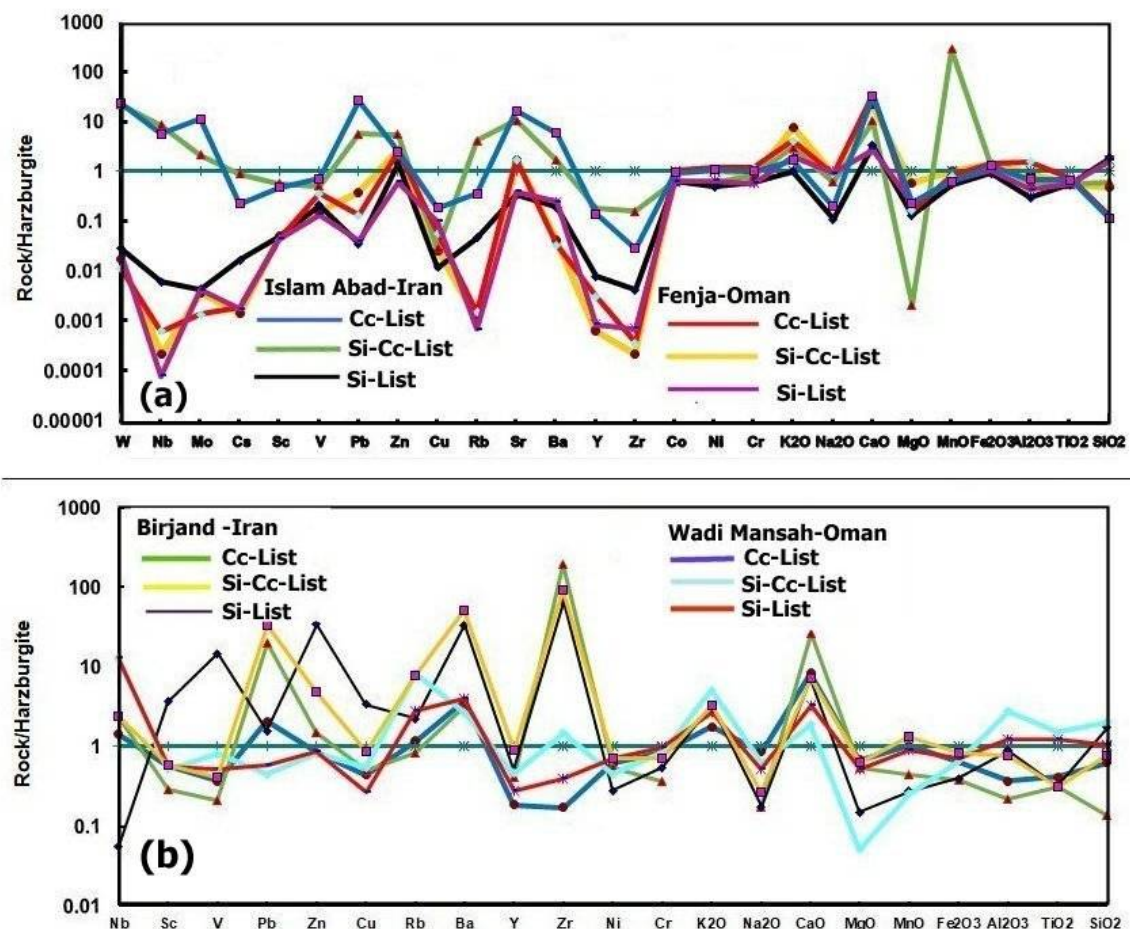


Figure 16. a-b. (a) Major and trace elements contents in Listwaenite lithologies from Fenja and Islam Abad area normalized by harzburgite from Fenja area, compared to Listwaenite lithologies from Birjand ophiolite in Iran [26] and Wadi Mansah in Samail ophiolite [17] (Figure. 16b). Cc-List: carbonate listwaenite, Si-Cc-List: Carbonate-Silica listwaenite, Si-List.: Silica listwaenite.

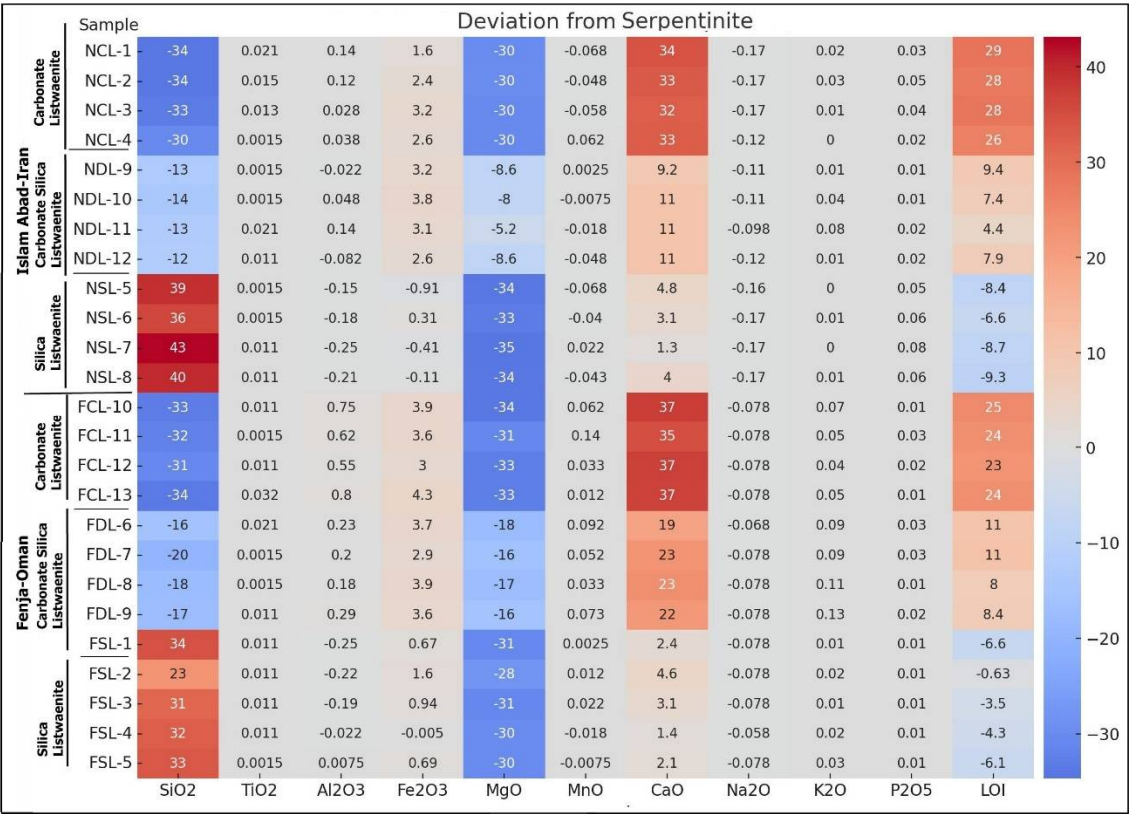


Figure 17. a. Positive and negative deviation of major elements in listwaenites relative to serpentinite.

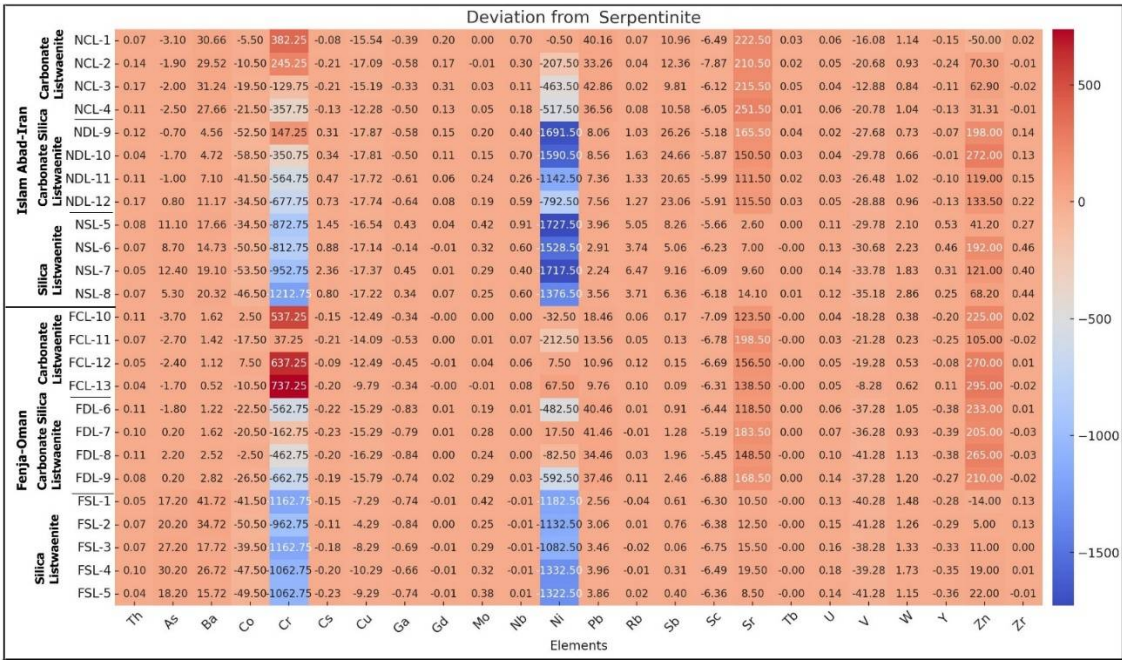


Figure 17. b. Positive and negative deviation of trace elements in listwaenites relative to serpentinite.

6.2. Origin of Listwaenites in Oman and Iran

Whole rock major and trace elements analysis, mineralogy and textural evidence indicate that the protolith of the investigated listwaenites were serpentinitized mantle harzburgites and serpentinites, similar to those outcropping elsewhere in the ophiolite in Oman and Iran. In general, the harzburgites underwent an advanced alteration that resulted in their becoming serpentine in the first stage and listwaenites in the second.

The presence of quartz and carbonate-rich listwaenites is thought to be caused by an increase in CO₂, CaO, and SiO₂ through hydrothermal fluids, which also alters the associated serpentinites and serpentinitized harzburgite (Figure.13). These high values of CaO, MgO, SiO₂, and LOI in the listwaenites are hypothesized to have occurred during hydrothermal alteration. According to Spiridonov [42] the alteration process comprises the replacement of silicates in ultramafic rocks with carbonate and silica where olivine and pyroxene in the ultramafic rocks donate the bivalent metal cations Fe, Mg. The relative concentration of clinopyroxene in the parent rock and the input of Ca in the hydrothermal fluid determine how the amount of Ca in the carbonate. Silica is liberated to form quartz as a result of the dissolution of the silicates and the fixing of Fe-Mg-Ca in carbonates [4,13,43]. Figure. demonstrated that SiO₂ and MgO have a negative association. This suggests that magnesium oxide has been removed from the environment with the introduction of hydrothermal fluids containing CO₂ and the onset of listwaenitization processes. This is related to the high absorption of CO₂ in harzburgite and serpentinites. These rocks have the capacity to produce surface carbonate, as demonstrated by their high absorption [44].

According to Esfandiari et al. [45], carbonate listwaenites are formed in the first stage of serpentinite alteration processes, followed by carbonate-silica listwaenites and silica listwaenites in the final stage. These conclusions are based on the temperature and pressure conditions required for the formation of carbonate and silica. The existence of three distinct Listwaenite types could be explained by variations in the protolith's mineralogical and geochemical characteristics as well as by various stages of hydrothermal alteration that result in various stages of metasomatic replacement. Different types of listwaenites may arise because of fluctuations in pH, temperature, and CO₂ fugacity. According to Ash and Arksey [46] and Uçurum [4], carbonate listwaenites form at high CO₂ fugacity, pH range of 8–10, and moderate–high temperature. At high alkalinity conditions (pH > 11), primary silicate minerals lost material and created zones of high porosity, which led to the development of carbonate listwaenites [2,47]. Different pH and CO₂ fugacity ranges may result in the formation of silica-carbonate listwaenites [e.g., 12]. For a stable quartz-dolomite assemblage with xCO₂ values varied between 0.1 and 0.5 at 1 kbar, a maximum temperature ranges of 350 to 400 °C is recommended [48]. After the mostly serpentine minerals dissolved during the first carbonate phase of alteration, silica listwaenites were created in the last stage by the precipitation of Si from the circulating hydrothermal fluids. Listwaenite gets a yellow-brown tint as a result of limonite development brought on by weathering and oxidation of Fe-oxides produced during serpentinitization.

Islam Abad Listwaenite has a greater trace and REE element content than Fanja Listwaenite. According to Qiu & Zhu's [49], trace element abundance in Listwaenite rises as shear zone deformation advances. This suggests that increased deformation occurrences are connected to the rise in trace elements in the Islam Abad listwaenites. Carbonate in Listwaenite developed at 80–130 °C [17] or 50–250 °C [28] according to values of clumped isotopes and mineral paragenesis. While there is some overlap, these temperatures are often higher than the <65 °C anticipated temperatures for Listwaenite formation [50]. Most of the pressure during the creation of Listwaenite remains unknown. Falk and Kelemen [17], however, employed typical subduction-zone geotherms and hypothesized that Listwaenite might have formed at pressures between 0.2 and 1.5 GPa based on the theory that the mineral developed in a subduction-zone scenario. At these pressures, the CO₂ concentration necessary to stabilize the magnesite + quartz assemblage is only slightly higher than seawater CO₂ concentrations. Equilibration of released water with carbonate in subducted sediments can yield fluids with sufficiently high CO₂ concentrations to form magnesite-quartz Listwaenite upon reaction with harzburgites and the mass of fluid produced by compaction and partial dehydration reactions is sufficient to account for the observed mass of Listwaenite. These calculations are applicable to subduction zones worldwide. Globally, extensive carbonation of mantle wedge peridotite may be more common above subduction zones at the "leading edge of the mantle wedge" than has been previously recognized.

7. Conclusions

Islam Abad and Fanja listwaenites were formed due to hydrothermal alteration of serpentinitized harzburgites and serpentinites along thrust faults and shear zones which acted as pathway for fluids. There are three distinct types of listwaenites: carbonate-, silica-carbonate-listwaenites, and silica-

listwaenites. The higher trace elements contents in the Islam Abad listwaenites suggests that the degree of deformation in Islamabad area in Iran has been higher than the Fanja area of Oman. The ultramafic protolith is further supported by petrographic observation and by the enrichment mode of Cr, Ni, and Co in the listwaenites. The listwaenites alteration process occurred after the harzburgite suite serpentinized and the upward circulation of CO_2 , CaO, SiO_2 , and Fe_2O_3 rich hydrothermal fluids along fault zones. The alteration process is isocheimal in terms of the major and trace elements that are redistributed at different scales, with the exception of K, CO_2 , H_2O , Mg, Ca, and Si.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Supplementary file S-1. Detection limit and quality control of chemical analysis. Supplementary file S-2. Average of listwaenites from Oman and Iran Supplementary file S-3a-e. Correlation matrix of major oxides and trace elements in the listwaenite from Fenja and Islam Abad area.

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