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Evolution and economic significance of listwaenites associated with Neoproterozoic ophiolites in South Eastern Desert, Egypt

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⊣ **A B S T R A C T** ⊢

Most South Eastern Desert ophiolites are found along the Allaqi-Heiani-Gerf suture along the Egypt-Sudan border. Serpentinites, altered slices of upper mantle, are the main components of this suture and other sutures in the Arabian-Nubian Shield. Listwaenites are a distinctive alteration of serpentinized peridotite and are commonly found in shear zones that concentrate hydrothermal fluids involved in the formation of this type of rock. Along Wadi Allaqi area, listwaenites are distinguished into two main types: i) silica-rich, and ii) carbonate-rich. The presence of fuchsite in the former indicates that it is typical listwaenite, while the absence of fuchsite in the latter indicates listwaenite-like rock. These two types of listwaenites represent different stages of hydrothermal alteration. The large variations in their mineralogical and geochemical compositions are due to the different influence of reactions between protoliths and hydrothermal solutions, leading to different stages of metasomatic replacement. Ore minerals accompanying the listwaenites vary greatly both among and within separate occurrences. These variations depend on lots of factors, including the presence of shearing, P-T conditions, reactions with host rocks, and the composition of the hydrothermal fluids. Silica-rich listwaenite is well sheared and is more commonly ore bearing, while carbonate-rich listwaenite is less obviously sheared and shows less metal enrichment. The listwaenites of Wadi Allaqi area have a potential for gold mineralization (4-12ppm; 400-1100x enriched in comparison with serpentinites) since native gold occurs as inclusions in pyrite or as small disseminated specks along fractures. Base metals, mostly copper, lead and zinc, are also associated with listwaenites, but are more erratically distributed. Gold content increases with increasing SiO_2 content of listwaenite. Carbonatization and silicification of ophiolitic peridotites can concentrate gold in the alteration products more than the parent rocks.

KEYWORDS | Arabian-Nubian Shield. Neoproterozoic. Ophiolite. Serpentinite. Listwaenite. Fuchsite. Gold.

INTRODUCTION

Ophiolites are key components of the Neoproterozoic Arabian-Nubian Shield, providing important clues about its origin and mineralization. In the Arabian-Nubian Shield, ophiolites are often pervasively altered due to the

migration of solutions of diverse compositions (Stern and Gwinn, 1990; Azer, 2008). The migration of these solutions also resulted in a diffuse and pervasive carbonation and silicification of a wide range of Neoproterozoic rocks of the Arabian-Nubian Shield. Although we are not yet able to quantify the volume of carbonate added to the crust

of this region, it is clear that vast amounts of such fluids accompanied the greenschist-facies metamorphism of a large portion of the Arabian-Nubian Shield. The source and age of this pervasive carbonate alteration in the Arabian-Nubian Shield and in other Neoproterozoic crustal tracts is controversial but is important for understanding fundamental as-pects of Earth evolution (Santosh and Omori, 2008). Carbonate alteration of Arabian-Nubian Shield ophiolites formed listwaenite, particularly in the shear zones.

Listwaenite is an assemblage of carbonate minerals (magnesite, ankerite and dolomite), quartz and/or fuchsite (Cr-muscovite) together with disseminated sulfides and accessory minerals (Halls and Zhao, 1995). Various spellings appear for the term in the geological literature, including listwaenite, listwanite, listvanite and listvenite However, the term "listwaenite" is now commonly used by geologists for carbonated and/or silicified mafic-ultramafic rocks and will be used in this work. Recently, listwaenite drew the attention of geologists because of their worldwide association with gold mineralization (*e.g.*, Barnes *et al.*, 1973; Buisson and Leblanc, 1985, 1986; Ash and Arksey, 1990; Aydal, 1990; Koç and Kadıolu, 1996; Uçurum and Larson, 1999; Uçurum, 2000). In other situations, a spatial and genetic relationship has been observed between carbonatized ultramafics and the distribution of gold and talc deposits. Apparently, carbonatization concentrates gold up to a thousand times that of the original ultramafic rocks (Cox and Singer, 1986; Bussion and LeBlanc, 1987).

Listwaenite has long been appreciated as part of Egyptian Neoproterozoic rocks, but has been referred to as "talc-carbonate rocks" (Amin, 1948) or "Barrimaya Rock" (Hume, 1934). Because of rising interest in gold mineralization in Egypt, Egyptian listwaenites are now receiving more attention (*e.g.*, Oweiss *et al.*, 2001; Ramadan, 2002; Azer, 2008; Zoheir, 2008a). There has been no substantial study of listwaenite occurrences in the Eastern Desert of Egypt to date, despite the fact that in other similar Neoproterozoic ophiolitic terranes (*e.g.*, Morocco, Saudi Arabia) similar listwaenites are associated with potentially economic gold concentrations (Buisson and Leblanc, 1985, 1987). The present work studies for the first time the occurrence of listwaenites associated with the ophiolitic rocks of Wadi Allaqi area. This study presents the geological, mineralogical and geochemical characteristics of the listwaenites to discuss their genesis and evolution as well as their precious metal content. The new data are used to better understand gold mineralization in the South Eastern Desert of Egypt. We hope this work encourages other researchers to begin studying listwaenites in the Eastern Desert of Egypt, so that the economic significance of these rocks can be better assessed.

GEOLOGICAL BACKGROUND

Regional Geology

Neoproterozoic ophiolites are common in the central and southern sectors of the Eastern Desert of Egypt (Fig. 1). Egyptian ophiolites consist of a lower unit of serpentinized ultramafic rocks and an upper unit of layered and isotropic gabbro, sheeted dykes and pillowed basalt (El Sharkawy
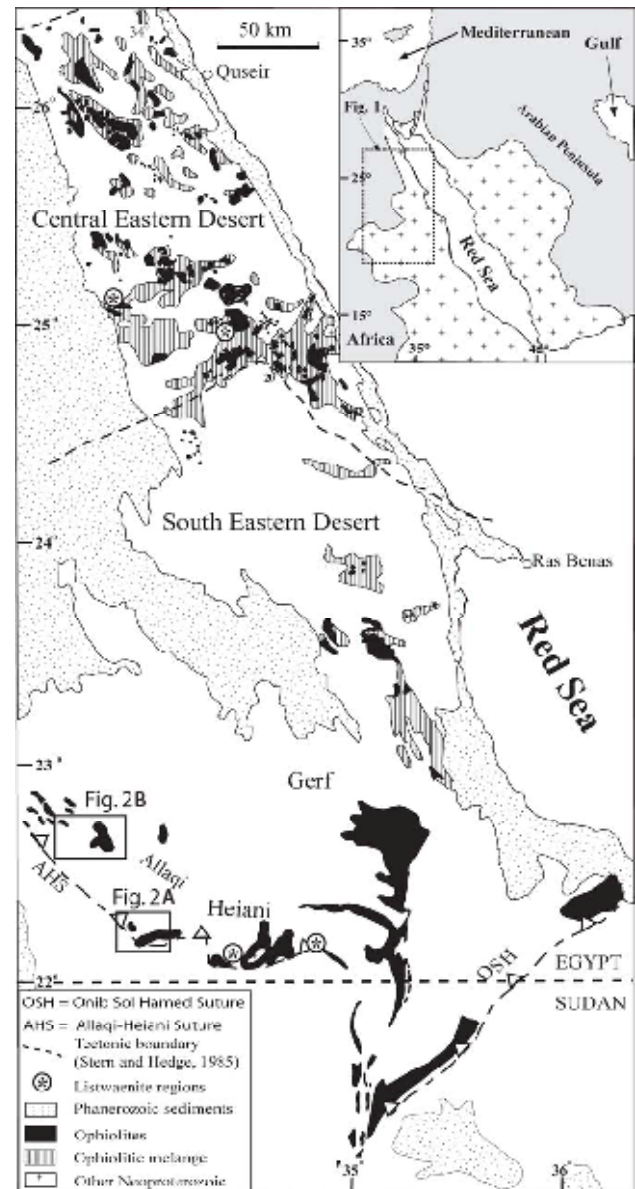

FIGURE 1 | Distribution of ophiolitic rocks in Eastern Desert of Egypt (modified after Shackleton, 1994) and location of Figure 2A, B is indicated. Generalized regions for listwaenite in the Eastern Desert of Egypt are indicated (Osman, 1995; Oweiss, 2001; Ramadan, 2002; Zoheir, 2008a; Zoheir and Lehmann, 2011). Inset shows the location of the Eastern Desert in the northernmost Arabian-Nubian Shield Neoproterozoic exposures location of Figure 1.

and El Bayoumi, 1979). However, because of folding and shearing, most Egyptian ophiolites lack one or more of their diagnostic lithologies. All Egyptian ophiolites are strongly deformed and metamorphosed. Low-grade greenschist facies metamorphism predominates, but in some places the rocks reach amphibolite grade. Ophiolitic peridotites were altered by large volumes of fluids of diverse composition, resulting in serpentinization, silicification and carbonatization (*e.g.*, Stern and Gwinn, 1990; Azer, 2008).

Most south Eastern Desert ophiolites are found along the Allaqi-Heiani-Gerf suture zone, from Lake Nasser to the Red Sea. This is the western part of a much longer ophiolite-decorated suture zone, the Ess-Yanbu-Onib-Sol Hamed-Gerf-Allaqi-Heiani Belt (YOSHGAH suture of Stern *et al.*, 1990) which trends from the eastern edge of the northern Arabian shield to Lake Nasser. The Ess-Yanbu-Onib-Sol Hamed-Gerf-Allaqi-Heiani suture is considered, along with the Ariab-Nakasib-Thurwah-Bir Umq suture farther South in Arabia and Sudan (Johnson *et al.*, 2004), to be one of the two longest and most complete Neoproterozoic ophiolite-belts in the Arabian-Nubian Shield. It was formed by the collision of the South Eastern Desert or Gerf terrane to the north with the Gabgaba or Gebeit terrane to the South (Kröner *et al.*, 1987) and is decorated by variably disrupted ophiolite fragments. Ali *et al.* (2010) suggested two evolutionary stages for the Ess-Yanbu-Onib-Sol Hamed-Gerf-Allaqi-Heiani Ophiolite Belt (~810-780Ma and ~730-750Ma) concluding that accretion between the Gabgaba-Gebeit-Hijaz terranes to the South and the South Eastern Desert-Midyan terranes to the north occurred as early as 730Ma and no later than 709Ma.

The Wadi Allaqi segment of the Ess-Yanbu-Onib-Sol Hamed-Gerf-Allaqi-Heiani suture separates the SE segment of the Eastern Desert terrane in the north from the Gabgaba terrane in the South (Abdelsalam and Stern, 1996). The Wadi Allaqi segment is broad and consists of gneiss, ophiolites, island arc assemblages and gabbroic to granitic intrusions (Stern *et al.*, 1990; Kröner *et al.*, 1992; Abd El-Naby and Frisch, 2002; Kusky and Ramadan, 2002; Abdelsalam *et al.*, 2003; Zoheir and Klemm, 2007; Ali *et al.*, 2010). The ophiolite assemblages comprise one or more nappes composed mainly of mafic-ultramafic rocks and slices of serpentinite and talc-carbonate. Stern *et al.* (1990) inferred that the Allaqi-Heiani ophiolitic nappe verged South during emplacement, and was then shortened E-W during terminal collision between E and W Gondwana at ~630Ma. The Wadi Allaqi segment hosts important mineral deposits, such as gold, chromite, magnesite and talc (Klemm *et al.*, 2001; Kusky and Ramadan, 2002; Oweiss *et al.*, 2001; Zoheir, 2008a).

Serpentinite represents the most distinctive lithology of dismembered Allaqi ophiolites. These contain relicts of fresh ultramafic minerals and show extreme alteration along thrusts and shear zones with the development of talc, talc-carbonate and reddish-brown quartz-carbonate rocks (listwaenites). Listwaenites were reported from some localities in the Eastern Desert of Egypt (Fig. 1) and are frequently associated with gold mineralization (Osman, 1995; Ramadan, 1995, 2002; Hassaan *et al.*, 1996; Oweiss *et al.*, 2001; Botros, 2004; Azer, 2008; Zoheir, 2008a, b; Zoheir and Lehmann, 2011).

Field description

Our study is concentrated on two localities in the Wadi Allaqi area referred to (from E to W) as Wadi Abu Fas and Jabal Shilman (Fig. 2A, B).

Wadi Abu Fas area

The main rock types in the Wadi Abu Fas area comprise mafic-ultramafic rocks, island arc-related assemblages, and syn-orogenic granodiorite (Fig. 2A). The mafic-ultramafic suite of Wadi Abu Fas is one of the largest mafic-ultramafic occurrences in the South Eastern Desert (~75km^2). It was considered to be an arc-related layered intrusion (Sadek and El-Ramly, 1996) or an ophiolitic sequence (Ali *et al.*, 2010). In Wadi Abu Fas area, the mafic-ultramafic rocks are represented mainly by serpentinites and layered metagabbros as well as minor exposures of pyroxenite and pyroxene-rich peridotite. The mafic-ultramafic rocks show extreme alteration along thrust and shear zones with the development of quartz-carbonate rock (listwaenite). Relics of less-altered ultramafic rocks are found in the lower parts of the serpentinites of Wadi Abu Fas. Metapyroxenites are occasionally encountered as small lenses within the Wadi Abu Fas serpentinites, while pyroxene-rich peridotite occurs as elongated dykes. Gabbroic rocks are mainly isotropic or layered metagabbros and gave an age of 730±6Ma (Ali *et al.*, 2010) similar to that of ophiolitic rocks in the central Eastern Desert. Arc metavolcanic rocks in the Wadi Abu Fas area are metamorphosed to greenschist facies (El-Nisr, 1997). Metasedimentary rocks found in the area consist of marble, schist, greywacke and subordinate conglomerate (El Gaby *et al.*, 1988).

Listwaenites in the Wadi Abu Fas area are easily distinguished from other rocks due to their yellow-brown colors and positive relief relative to the country rock. They occur as ridges (Fig. 3A) as well as in the form of irregular lenses (Fig. 3B) along fault zones between ultramafic rocks and island arc assemblages. Listwaenite ridges reach up to several hundred meters in length and are up to 20m wide. Listwaenite lenses reach
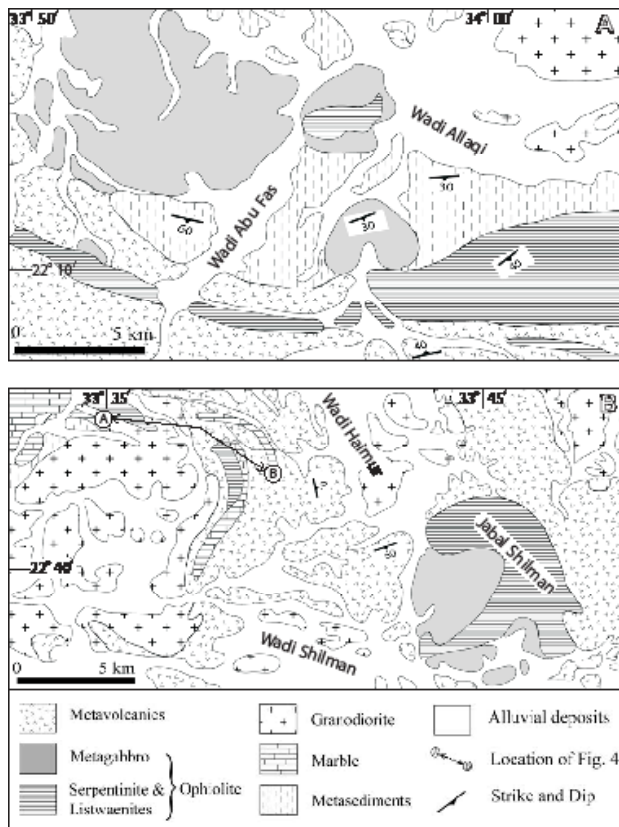
FIGURE 2 | Detailed geological maps of the study areas (after Ali *et al.*, 2010): A) Wadi Abu Fas area and B) Jabal Shilman area. A-B: Approximate location of the cross section of Figure 4.

up to 5m in length parallel to the regional foliation and to the enclosing shear zones. Contacts of istwaenite with country rocks are sharp and regular.

Jabal Shilman area

The main rock types in the Jabal Shilman area are represented by ophiolitic rocks, metasedimentary rocks including marble, metavolcanics and syn-orogenic granodiorite (Fig. 2B). The ophiolitic rocks define the northwestern continuation of the Allaqi-Heiani ophiolite belt (Kröner *et al.*, 1987). They are overlain by the arc metavolcanic–metasedimentary succession and intruded by granodiorite. The ophiolitic rocks include completely serpentinized peridotite, talc-carbonates, metagabbros and amphibolites that were subsequently metamorphosed to greenschist and amphibolite facies (Mansour *et al.*, 1998; Abd El-Naby *et al.*, 2000; Abdeen and Abdelghaffar, 2011). The largest serpentinite mass occurs at Jabal Shilman forming a thrust nappe, which is also associated with a large metagabbro body. Two small serpentinite masses occur in the north-western part of the study area and are closely associated with marble and listwaenite. The serpentinite masses in the north western part of the

mapped area are intruded by granodiorite. Kröner *et al.* (1992) obtained single zircon $^{207}Pb/^{206}Pb$ evaporation ages of 729±17Ma and 736±11Ma for metagabbro and metadiorite associated with serpentinites, respectively. The amphibolite is a metamorphosed dismembered ophiolitic fragment of layered metagabbro. It consists of mafic bands rich in hornblende alternating with felsic bands rich in plagioclase. Arc metavolcanics are represented mainly by meta-andesite and meta-dacite; a sample of the latter gave a U-Pb zircon SHRIMP age of 733±7Ma (Ali *et al.*, 2010). Syn-tectonic granitoids include granodiorite, interpreted as arc-related and I-type (El-Kazzaz and Taylor, 2001), which gave a U-Pb zircon SHRIMP age of 629±5Ma (Ali *et al.*, 2010).

Listwaenites of the Jabal Shilman area form ridges (Fig. 3C) due to their resistance against weathering relative to the surrounding rocks. They are found along the tectonic contacts of the serpentinite with the metavolcanics and granodiorite intrusion (Fig. 4). Listwaenites have brecciated textures in the outcrops and dense, hierarchical fracture networks extending to microscopic scales, filled by carbonate and quartz veins. The listwaenites of Jabal Shilman are classified into two types: silica-rich and carbonate-rich listwaenites; the latter is more common. They crop out as yellowish- to reddish-brown weathering carbonate with fine ribbons of quartz weathered out on the surface. Silica-rich listwaenite is well sheared and cracked, while carbonate-rich listwaenite has limited cracks and fissures. The carbonate-rich listwaenite is cut by numerous small quartz veins formed after emplacement of the listwaenite. Metasedimentary rocks in Jabal Shilman area are represented by gneiss and marble.

ANALYTICAL TECHNIQUES

Several listwaenite samples as well as serpentinites were subjected to X-ray powder diffraction (XRD) analysis to determine their mineralogical composition. The powder diffraction pattern of the samples was obtained with Cu radiation with secondary monochrometer. The scanning speed was 2θ= 1deg/min at constant voltage 40kV and 40mA using a BRUKER D8 advanced X-ray diffractometer at the central Metallurgical and Development Institute in Cairo, Egypt. Mineral identification was carried out using the data given in the American Standard Test Materials (ASTM) cards by measuring the d-values of the different atomic planes and their relative intensities.

Polished sections of selected samples of listwaenite were examined with a Philips XL30 environmental scanning electron microscope (ESEM), operating at 25kV and equipped with EDAX energy dispersive
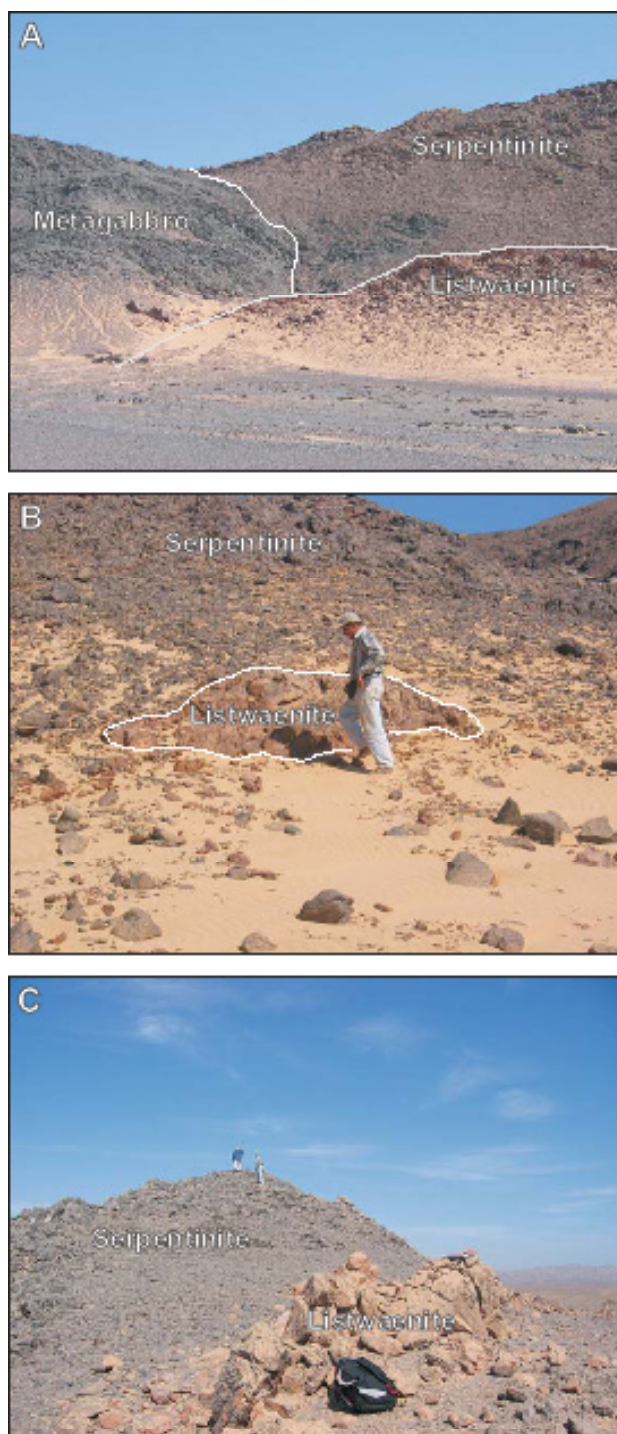
Whole-rock chemical analyses of powdered rock samples (11 listwaenites and 4 serpentinites) from the study areas were carried out at ACME Analytical Laboratories (Canada) for major oxides, trace elements and REE. Major oxides compositions and Sc, Ba, and Ni elements were analyzed using Inductively Coupled Plasma-Emission Spectrometry (ICP-ES). The remainder of trace elements and the rare earth elements (REE) were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) following a lithium metaborate/tetraborate fusion and nitric acid digestion of a 0.2g sample. In addition, a separate 0.5g split was digested in Aqua Regia and analyzed by ICP-MS to determine abundances of precious and base metals. The detection limits for major oxides are between 0.001 to 0.04wt.%, while the detection limits for trace elements are between 0.01 and 0.5ppm. Analytical precision, as calculated from replicate analyses, is 0.5% for major elements and varies from 2% to 20% for trace elements. Loss on ignition (LOI) is determined by weight difference after ignition at 1000ºC.

PETROGRAPHY AND MINERALOGY

Petrographic studies were carried out on both thin and polished sections of the host rocks (serpentinites) and the listwaenites. The mineral contents of listwaenites and serpentinites were determined by XRD and optical microscopy. Also, the ESEM technique was used to identify some accessory minerals in the listwaenites (fuchsite, gold, pyrite, spinel and magnetite) to support the microscopic identification.

Petrographic studies indicate that the mineralogical compositions of listwaenites change both among and within separate occurrences. For this reason, the listwaenites were classified into two sub-groups based on their SiO_2 contents: silica-rich listwaenite (>40% quartz) and carbonate-rich listwaenite (>60% carbonate). Listwaenite of Wadi Abu Fas area is carbonate-rich listwaenite, while in Jabal Shilman area both silica-rich listwaenite and carbonate-rich listwaenite are recorded. Silica-rich listwaenites are yellowish-brown and consist mainly of silica and carbonates together with subordinate fuchsite and opaque minerals with accessory antigorite, talc, and kaolinite. XRD data reveals that the carbonates include magnesite and dolomite as well as minor calcite and ankerite. The presence of fuchsite in the silica-rich listwaenite indicates that it is typical listwaenite (Halls and Zhao, 1995, Akbulut *et al.*, 2006). Carbonate-rich listwaenites are reddish-brown and brown in hand specimens and composed mainly of carbonates with variable amounts of quartz (<20%), kaolinite, antigorite, talc, and minor opaque minerals. XRD data

FIGURE 3 | A) Listwaenite ridge associated with mafic-ultramafic rocks in Wadi Abu Fas area, B) Lens of listwaenite associated with serpentinite in Wadi Abu Fas area, and C) Listwaenite ridge associated with serpentinite in Jabal Shilman area.

analytical X-ray sensitivity. The spectrometer detects elements with atomic number greater than 4 (*e.g.*, B) and a counting rate (per second) close to 1000-1500 counts per second. The ESEM analyses were carried out at the Nuclear Materials Authority in Egypt.
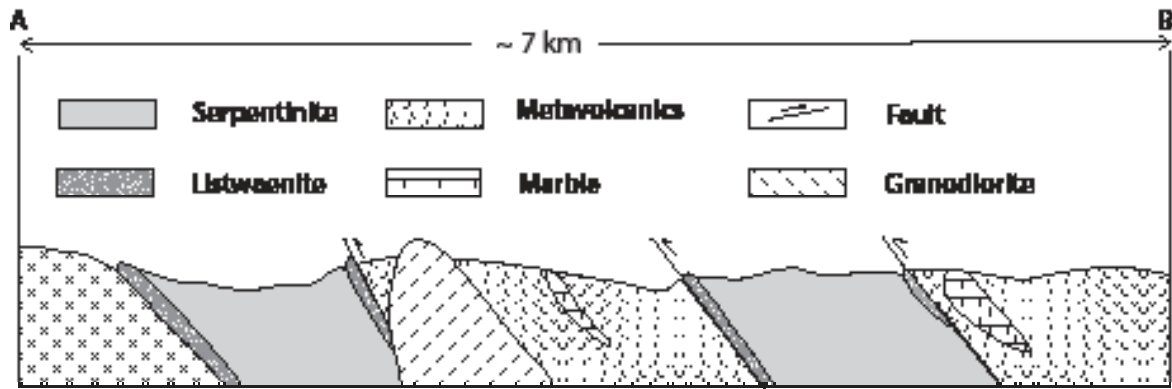
FIGURE 4 | Schematic cross section showing the relationship between the listwaenites and their host rocks at Jabal Shilman area.

reveals that the carbonates are represented mainly by calcite with minor amounts of magnesite, dolomite and ankerite. The absence of fuchsite in the carbonate-rich listwaenite indicates that it is a listwaenite-like rock (Halls and Zhao, 1995; Akbulut *et al.*, 2006).

The serpentinites in the Wadi Abu Fas and Jabal Shilman areas include massive and sheared varieties. Mineralogical composition of the serpentinites in both localities is similar. Along shear zones, listwaenite overprints the texture of the serpentinites indicating that listwaenite formed after emplacement of ophiolitic rocks. XRD data reveals that the most common serpentine phases are antigorite together with lesser chrysotile and lizardite as well as minor magnesite and brucite. Massive serpentinites commonly preserve crystal habits of orthopyroxene and olivine as well as the original rock texture, indicating harzburgite and dunite composition of the parent rocks. Pseudomorphs of orthopyroxene are revealed by the presence of bastite texture, while olivine is indicated by the presence of mesh texture. The sheared serpentinites have the same mineralogical composition as the massive serpentinites, but the minerals in the former are commonly arranged in subparallel alignment producing schistosity.

Ore microscopic studies revealed that the silica-rich listwaenites are richer in the opaque minerals (4-7% of the rock) than the carbonate-rich listwaenites (less than 2% of the rock). Primary opaque minerals in the silica-rich listwaenites are pyrite, chalcopyrite, cobaltite, magnetite, chrome spinel and gold. Secondary opaque minerals include covellite, goethite, malachite, and magnetite which resulted from surficial oxidation. Native gold was observed as ~5 micron inclusions in the pyrite (Fig. 5A) or as small specks (~20 micron; Fig. 5B). Pyrite occurs as fine cubic crystals (50 to 250μm; Fig. 5C) or as subhedral crystals altered to limonite along the crystal margins. Sometimes, pyrite grains are completely altered to goethite (Fig. 5D); lepidocrocite is present as a rim around goethite. Chalcopyrite is less abundant than pyrite and altered to

covellite (Fig. 5E). Cobaltite forms coarse crystals (200 to 250μm), displaying a perfect hexagonal basal section (Fig. 5F). Chrome spinel occurs as anhedral and subhedral crystals displaying a cataclastic texture, especially in the large crystals. Minor magnetite was observed as primary and secondary phases. Primary magnetite occurs as euhedral fine crystals, while secondary magnetite occurs as narrow rims at the margins and along the fractures of the chrome spinels. The carbonate-rich listwaenites contain minor amounts of opaque minerals and they are represented by magnetite, pyrite, goethite, chromite and hematite.

GEOCHEMICAL CHARACTERISTICS

Representative chemical analyses of 11 listwaenites and 4 serpentinites from the Jabal Shilman and Wadi Abu Fas areas are given in Table 1. The transformation of serpentinites to listwaenites with different chemical and mineral assemblages involves changes in the concentrations of the major oxides and trace element contents of the rock. The listwaenites show a wide variation in the major and trace elements. It is apparent that SiO_2, Fe_2O_3, MgO and CaO are the most variable major oxides in the analyzed rocks (Fig. 6A, B), although Mg#=100Mg/(Mg+Fe) is indistinguishable between listwaenites and serpentinites of Wadi Abu Fas. The silica-rich listwaenite has higher SiO_2 content (average 47.58wt.%) than the serpentinites (average 36.91wt.%), while the carbonate-rich listwaenite has lower SiO_2 content (average 23.66wt.%). Silica-rich listwaenite is also enriched in Na_2O and K_2O in relation to serpentinites or carbonate-rich listwaenite. Listwaenites are depleted in Cr, Ni and Co in comparison to serpentinite, but on the contrary listwaenites are relatively enriched in Au, Ag, As, Sb, Cu, Zn and Rb. Serpentinites have lower LOI values (12.70-17.40wt.%) than silica-rich listwaenite (17.61-21.10wt.%) and carbonate-rich listwaenite (28.31-31.10wt.%), consistent with their mineralogical compositions.

The carbonate-rich listwaenites that have limited cracks and fissures do not show metal enrichment such as sheared
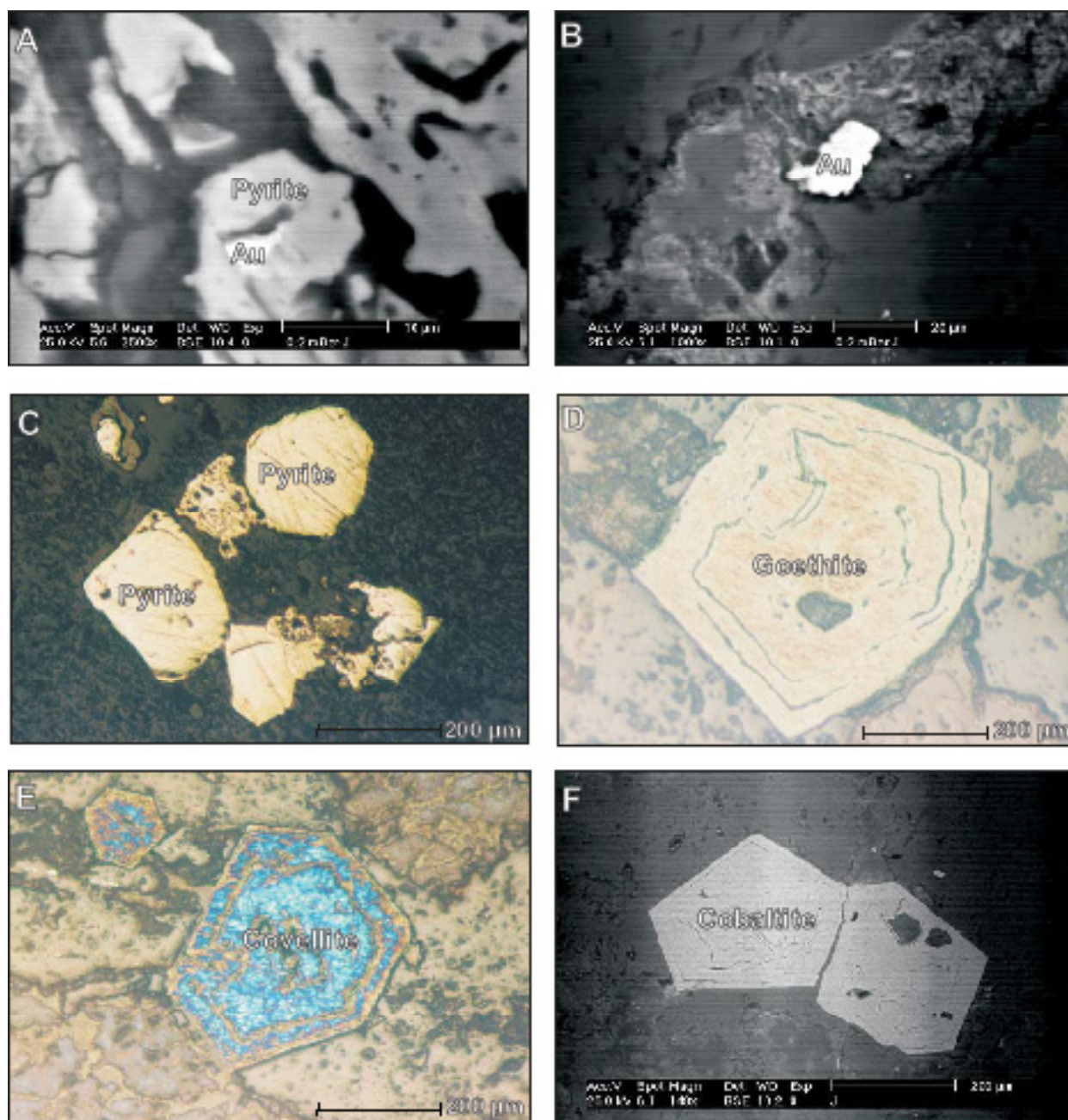
FIGURE 5 | A) Environmental scanning electron microscope (ESEM) image showing native gold as inclusion in the pyrite, B) ESEM image showing disseminated native gold in the silica-rich listwaenite, C) Pyrite crystals of silica-rich listwaenite in the polished surface, D) Pyrite crystal in the polished surface completely altered to goethite, E) Chalcopyrite in the polished surface altered to covellite, and F) Cobaltite in the polished surface forms euhedral crystals.

and cracked silica-rich listwaenites. Silica-rich listwaenites contain more SiO_2, Na_2O, K_2O, Au, As, Ag, Sb, Hg, Ni, Cr, Cu and Pb than the carbonate-rich listwaenites, but the latter contains more Al_2O_3, MgO, Fe_2O_3, and Ba. The chemical analyses of the present study indicate that gold content in the listwaenites increases in relation to the SiO_2 content (Fig. 7A). This is also consistent with the high quartz abundance observed in the thin-sections. These results are consistent with studies that point out that gold enrichment

is related to the introduction of silica (Buisson and Leblanc, 1985; Auclair *et al.*, 1993; Halls and Zhao, 1995; Uçurum, 2000; Akbulut *et al.*, 2006). In the present work, a positive correlation between Au and other chalcophile trace elements such as Ag, As, Sb, Cu, Zn and Pb (Fig. 7B) suggests that these elements can be used as indicators of gold mineralization.

Analyzed serpentinites show extremely low contents of K_2O, CaO, and Na_2O and high MgO, Fe_2O_3, Co, Cr and Ni

TABLE 1 | Chemical analyses of the studied listwaenites and serpentinites along Wadi Allaqi area

	Carbonate-rich listwaenite						Silica-rich listwaenite					Serpentinites			
	Wadi Abu Fas			Jabal Shilman			Jabal Shilman					Wadi Abu Fas		Jabal Shilman	
	AF-3a	AF-5	AF-10	SH-2	SH-3	SH-4a	SH-9a	SH-10a	HS-12	SH-14	SH-17	AF-1	AF-4	SH-6	SH-7
SiO₂	26.72	22.89	24.63	22.57	20.68	24.29	50.32	46.94	48.07	45.03	47.55	37.71	36.22	36.55	37.16
Al₂O₃	2.71	2.95	2.86	2.01	1.45	1.59	1.53	1.15	0.88	1.19	1.03	2.39	2.27	0.22	0.39
Fe₂O₃(T)	8.11	7.85	8.93	9.13	11.58	10.27	3.98	4.73	5.37	4.59	4.98	11.25	13.40	6.47	7.27
MgO	16.94	19.93	18.53	20.50	21.39	24.39	12.97	13.72	14.04	13.90	13.97	34.86	34.55	37.41	38.34
CaO	15.86	17.00	15.27	14.07	13.85	7.74	10.83	10.75	8.90	11.75	10.33	0.51	0.37	0.34	0.25
Na₂O	0.04	0.03	0.04	0.04	0.02	0.03	0.48	0.39	0.35	0.42	0.38	0.04	0.02	0.01	0.02
K₂O	0.09	0.11	0.07	0.06	0.09	0.06	0.55	0.58	0.52	0.63	0.49	0.01	0.02	0.02	0.01
TiO₂	0.14	0.14	0.09	0.04	0.06	0.05	0.12	0.07	0.07	0.09	0.08	0.06	0.07	<0.01	<0.01
P₂O₅	0.01	0.01	0.02	<0.01	0.05	0.06	0.05	0.04	0.04	0.06	0.05	0.03	0.04	<0.01	0.01
MnO	0.15	0.16	0.12	0.11	0.13	0.12	0.23	0.29	0.55	0.12	0.34	0.15	0.14	0.08	0.07
Cr₂O₃	<0.002	0.002	0.003	0.002	<0.002	<0.002	0.04	0.05	0.063	0.071	0.063	0.163	0.150	0.223	0.225
LOI	28.31	28.40	28.60	30.40	29.80	31.1	17.61	19.67	20.90	21.10	19.90	12.90	12.70	17.40	15.30
Total	99.08	99.47	99.36	98.93	99.10	99.7	99.01	98.58	99.76	98.35	99.17	100.07	99.95	98.72	99.05
Mg#	80.54	83.42	80.44	81.547	78.54	82.47	86.59	85.18	83.82	85.71	84.75	85.99	83.63	91.97	91.27
Trace elements (ppm)															
Sc	8	5	5	6	3	6	5	7	6	6	6	22	25	34	29
Ba	127	247	250	334	159	137	146	131	127	110	102	23	22	48	49
Co	14.3	16.4	11.2	14.6	22.5	17.8	23.9	19.7	41.3	33.4	36.9	109.8	128	95.6	97.4
Hf	2.9	2.8	2.7	2.6	2.1	2.3	2.8	3.1	<0.1	<0.1	<0.1	0.3	0.2	0.4	0.2
Nb	0.4	0.3	0.2	0.5	<0.1	0	0.3	0.1	0.2	<0.1	0.1	3.5	2.9	4.2	3.5
Rb	91	96.8	93	107.9	89.2	98.6	26	25	12.1	16.6	18.5	2.1	2.5	2.4	2.5
Sr	197.8	217	220	226.7	201.3	175.9	211	203	186.2	210.6	197.8	117.5	120	176.3	179.9
Th	2.7	2.8	2.9	3.2	2.3	2.7	0.5	0.7	0.3	0.3	0.3	2.9	3.2	4.3	3.5
V	43	42	45	52	30	36.2	9	8	4	5	5	423	452	576	583
Zr	1.7	0.5	0.4	0.7	1.1	1.3	0.8	1	0.6	0.5	0.6	4.8	5.5	6.9	6.1
Y	3.1	3.9	3.6	5.1	4.3	4.6	3.1	2.6	0.9	2.1	1.9	2.3	2.8	2.5	3.1
Mo	1.4	1.7	0.9	1	1.5	1.4	1.1	0.8	0.6	0.5	0.5	0.1	0.3	0.4	0.5
Cu	78.8	87.6	72.1	98.5	94.6	96.4	174.7	182.8	213.4	197.9	309.7	43.2	44.3	57.8	58.6
Pb	46.1	46.5	45.8	42.3	34.1	38.7	116.5	111.6	115.5	156.3	119.7	20.3	21.4	36.6	30.5
Zn	38	39	36	50	32	46	123	106	167	111	139	25	24	23	24
Ni	83	85	84	45	96	71	86	95	116	105	87	960	925	1222	1226
As	151.2	112.3	92.1	80.7	101.2	91.2	957.4	836.7	995.5	740.7	663.1	1.5	2.1	2.6	1.9
Sb	30.5	21.3	41.4	25.5	30.9	27.5	157.8	109.4	167.8	150.1	140.6	<0.1	<0.1	<0.1	<0.1
Ag	3.1	3.0	2.9	2.8	2.7	3.1	4.4	3.9	4.0	3.5	3.5	0.1	0.1	<0.1	<0.1
Au	5	6	5	4	3	6	13	10	11	10	12	0.030	0.001	0.002	0.003
Hg	1.82	1.49	2.21	1.96	1.01	1.41	3.5	2.1	3.59	4.12	5.62	<0.01	<0.01	<0.01	<0.01

values. Serpentinite of Jabal Shilman has very low content of Al₂O₃ (0.29-0.39wt.%) and CaO (0.25- 0.34wt.%), and high Mg# (91.3-92.0). In contrast, Wadi Abu Fas serpentinite has high Al₂O₃ (2.27-2.39wt.%) and low Mg# (83.6-84.9) relatively to Jabal Shilman serpentinite. The Mg-numbers for the studied serpentinites are at the upper range of mantle peridotite Mg/(Fe+Mg) relation (Bonatti and Michael 1989). The high Mg# as well as very low abundances of Al₂O₃ and CaO of Jabal Shilman serpentinite make it similar to ophiolitic peridotites of the central Eastern Desert of Egypt (El Sayed *et al.*, 1999; El Bahariya and Arai, 2003; Farahat *et al.*, 2004; Azer and Khalil, 2005; Azer and Stern, 2007; Abd El-

Rahman *et al.*, 2009), but the lower Mg# of Wadi Abu Fas is more similar to peridotite of intrusive mafic-ultramafic rocks in the Eastern Desert and Sinai (Dixon, 1981; Khudeir, 1995; Khudeir *et al.*, 1996; Essawy *et al.*, 1997; Helmy and El Mahallawi, 2003; Azer and El-Gharbawy, 2011).

REE concentrations of the listwaenites and serpentinites are listed in Table 2. Average REE concentrations of these rocks normalized to chondritic values are plotted in Figure 8. The studied listwaenites show different REE patterns. These differences can be attributed to the fact that REE are likely to have been variably transported during formation of silica-
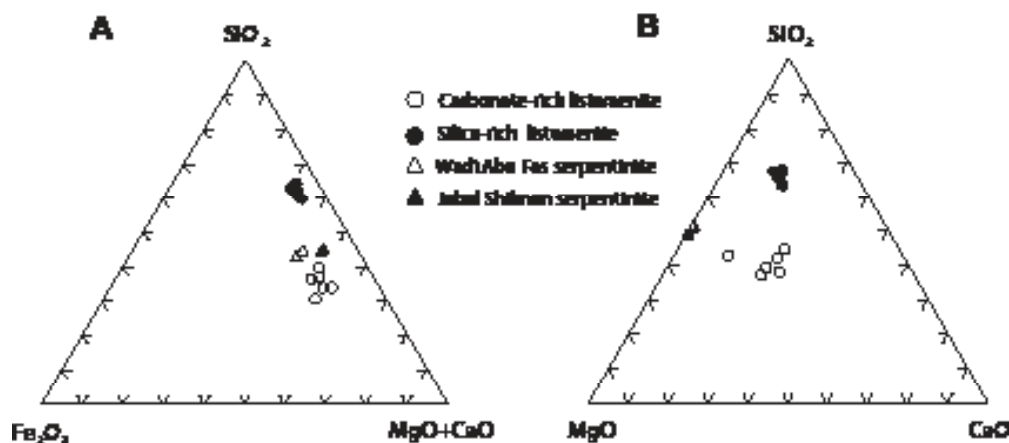
FIGURE 6 | Ternary diagrams for listwaenites and serpentinites (wt. %); A) SiO_2-Fe_2O_3-MgO+CaO, and B) SiO_2-MgO-CaO diagrams. This diagram was first included in the literature by Uçurum (1996).

and carbonate-rich listwaenites depending on the amount of carbonate and silica and/or different pH conditions. The silica-rich listwaenite contains significantly lower ΣREE (average 4.50ppm) than carbonate-rich listwaenite (average 50.04ppm) and serpentinites (average 7.42ppm). The listwaenites are characterized by moderate enrichment in light rare earth elements (LREE) relative to heavy rare earth elements (HREE) [$(Ce/Yb)_N$= 8.68-17.59]. The presence of goethite and calcite in the listwaenites may help account for the enrichment of LREE, given that these minerals can selectively absorb the LREE into their structures (Tsikouras *et al.*, 2006).

The serpentinites have different concentrations of REE and present different patterns. The serpentinites of Jabal Shilman have higher REE contents (average 10.22ppm) than those of Wadi Abu Fas (average 4.63ppm). REE content of the former have a slightly negative Eu-anomaly [$(Eu/Eu^*)_n$ =0.80-0.86] with a V-shaped pattern, which is typical for peridotite depleted ophiolite (Pallister and Knight, 1981). In contrast, REE of Wadi Abu Fas have a slightly positive Eu-anomaly [$(Eu/Eu^*)_n$ = 1.46-1.80] and a concave HREE pattern similar to the intrusive serpentinite of Kabr El Bonaya in South Sinai (Moussa, 2002) which indicates a different source than serpentinites of Jabal Shilman.

DISCUSSION

Listwaenite is commonly associated with gold mineralization in ophiolitic complexes worldwide (*e.g.*, Barnes *et al.*, 1973; Buisson and Leblanc, 1985, 1986; Ash and Arksey, 1990; Aydal, 1990; Koç and Kadıoğlu, 1996; Uçurum and Larson, 1999; Uçurum, 2000). However, the genetic connection between listwaenite and gold mineralization remains enigmatic. In Egypt, Neoproterozoic ophiolites are common in the central and

southern sectors of the Eastern Desert (Fig. 1), where they occur as tectonized bodies and mélanges of pillowed metabasalt, metagabbro, and variably altered ultramafic rocks. The latter are mostly serpentinites with relicts of fresh ultramafic protolith. The presence of listwaenites associated with serpentinites in several localities in the South Eastern Desert (Ramadan, 1995; Hassaan *et al.*, 1996; Oweiss *et al.*, 2001; Zoheir, 2008a, b; the present study) and central Eastern Desert (Osman, 1995; Ramadan, 2002; Botros, 2004; Zoheir and Lehmann, 2011) indicates that silicification and carbonation of the Egyptian ophiolite take place at a regional scale and extend for more than 500km from the northern to the southern end of the ophiolite exposures.

Alteration and metamorphism of the Egyptian ophiolites

The ophiolitic ultramafic rocks associated with the Egyptian ophiolites are generally highly altered, but it is often not known whether this alteration occurred before, during, or after emplacement. Thrust contacts are documented at the base of some, but not all, Egyptian ophiolites. An amphibolitic metamorphic sole at the base of the ophiolite is described at Wadi Haimur (Abd El-Naby *et al.*, 2000). Chloritites are developed around the peripheries of some ultramafic masses of the Egyptian ophiolites (Takla, 1991; Takla *et al.*, 1992).

The ultramafic rocks are largely converted to serpentinite and/or to mixtures of serpentine, talc, tremolite, chlorite, magnetite, and carbonates (Basta and Kader, 1969; Akaad and Noweir, 1972; Salem *et al.*, 1997; Ghoneim *et al.*, 1999, 2003). The origin of the carbonate alteration fluids remains to be elucidated, but Stern and Gwinn (1990) argued on the basis of C and Sr isotopic studies that pervasive carbonate alteration, affecting Egyptian ultramafic rocks, is a mixture of
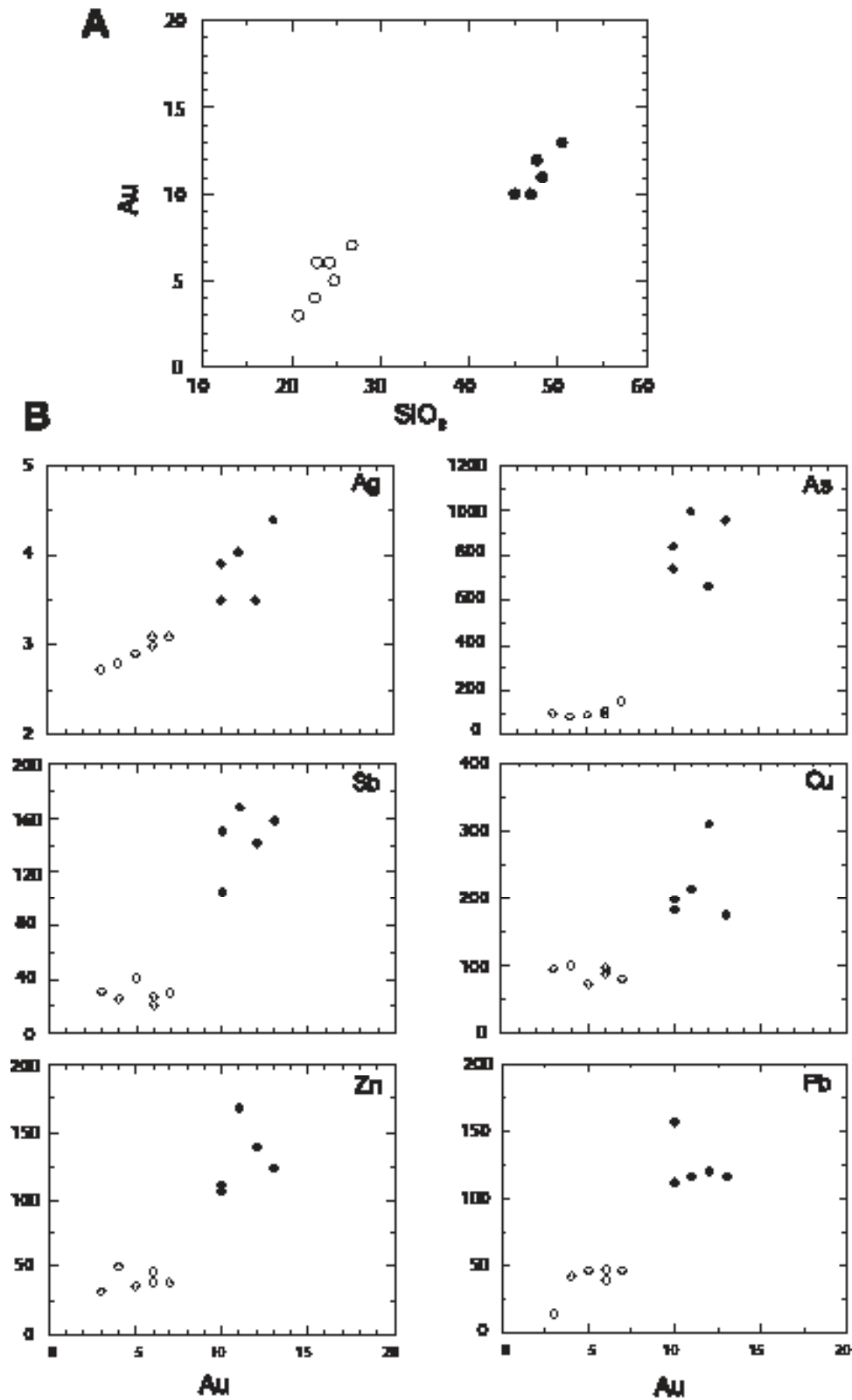
FIGURE 7 | A) Correlation of SiO$_2$ with Au in the studied listwaenites, B) Correlations of Au element with Ag, As, Sb, Cu, Zn and Pb in the studied listwaenites. Symbols as in Figure 6.

TABLE 2 | REE analyses (in ppm) of the studied listwaenites and serpentinites along Wadi Allaqi area

| | Carbonate-rich listwaenite | | | | | | Silica-rich listwaenite | | | | | Serpentinites | | | |
| | Wadi Abu Fas | | | Jabal Shilman | | | Jabal Shilman | | | | | Wadi Abu Fas | | Jabal Shilman | |
	AF-2a	AF-5	AF-10	SH-2	SH-3	SH-4a	SH-9a	SH-10a	HS-12	SH-14	SH-17	AF-1	AF-4	SH-6	SH-7
La	9.8	10.9	12.4	12.0	8.5	10.9	1.2	0.9	0.7	0.6	1.0	1.3	1.1	2.2	2.8
Ce	19.2	21.1	23.9	22.6	18.1	21.6	2.5	2.1	1.9	1.6	1.8	1.5	1.4	2.8	3.2
Pr	1.61	1.93	1.01	2.25	1.99	1.77	0.28	0.24	0.21	0.19	0.22	0.22	0.21	0.28	0.29
Nd	8.2	9.0	10.0	11.5	6.0	8.9	1.1	0.9	0.8	0.7	0.8	0.9	0.8	1.2	1.3
Sm	2.38	2.65	3.00	2.80	2.15	2.65	0.20	0.13	0.12	0.13	0.13	0.23	0.21	0.49	0.55
Eu	0.60	0.67	0.78	0.63	0.60	0.68	0.08	0.05	0.04	0.05	0.06	0.12	0.09	0.14	0.15
Gd	1.02	0.98	1.33	1.27	1.52	1.11	0.18	0.11	0.12	0.10	0.11	0.18	0.17	0.51	0.59
Tb	0.22	0.24	0.28	0.23	0.32	0.27	0.03	0.01	0.01	0.02	0.02	0.03	0.02	0.13	0.14
Dy	0.86	0.95	1.22	1.01	1.14	0.93	0.11	0.09	0.06	0.07	0.05	0.15	0.13	0.59	0.62
Ho	0.15	0.21	0.19	0.18	0.20	0.16	0.02	0.02	<0.02	<0.02	<0.02	0.03	0.02	0.09	0.11
Er	0.67	0.79	0.82	0.92	0.86	0.71	0.07	0.06	0.03	0.04	0.03	0.09	0.08	0.47	0.49
Tm	0.09	0.13	0.12	0.12	0.09	0.10	0.01	0.01	<0.01	<0.01	<0.01	0.02	0.01	0.04	0.05
Yb	0.49	0.61	0.65	0.70	0.50	0.54	0.08	0.06	0.03	0.04	0.05	0.11	0.09	0.47	0.53
Lu	0.08	0.10	0.12	0.11	0.09	0.10	0.01	0.01	<0.01	<0.01	<0.01	0.03	0.02	0.05	0.05
Sum	45.38	50.26	55.82	56.32	42.06	50.42	5.87	4.69	4.02	3.54	4.27	4.91	4.35	9.46	10.97
Eu/Eu*	1.18	1.27	1.19	1.02	1.01	1.21	1.29	1.28	1.02	1.34	1.53	1.80	1.48	0.86	0.80
(La/Sm)n	2.86	2.86	2.87	2.77	2.55	2.88	3.87	4.47	3.77	2.98	4.97	3.65	3.38	2.83	3.49
(Ce/Yb)n	10.88	9.81	10.21	8.97	10.08	11.11	8.68	9.72	17.59	11.11	10.00	4.88	3.79	1.85	1.70
(La/Yb)n	14.35	12.82	13.68	12.30	12.18	14.48	10.78	10.78	16.74	10.78	14.35	11.88	7.17	3.28	4.08
(Tb/Yb)n	2.04	1.79	1.98	1.49	2.91	2.27	1.70	0.78	1.52	2.27	1.82	1.14	1.24	1.31	1.18

mantle derived and remobilized sedimentary carbonate. The prevalence of carbonate alteration in Egyptian ophiolitic ultramafics certainly suggests the presence of a tremendous flux of CO_2-rich fluids coming from the mantle during middle and late Neoproterozoic time (Stern and Gwinn, 1990) or formed after serpentinization near the Earth's surface (Salem *et al*., 1997; Ghoneim *et al*., 1999, 2003). In contrast, Surour and Arafa (1997) argued that the 'ophicarbonates' of the Ghadir ophiolite are reworked oceanic calcites that formed after it was obducted.

Metallogenic specialization and importance of Egyptian ophiolites

In the Arabian-Nubian Shield, the strong association of ophiolites and mineralization emphasizes the importance of a better understanding of the nature, composition, and evolution of ophiolites. Arabian-Nubian Shield ophiolites host important mineral deposits such as chromite, magnesite, talc, platinum-group elements, Cu-Ni-Co mineralization and gold (Klemm *et al*., 2001; Kusky and Ramadan, 2002; Betros, 2004; Ahmed and Hariri, 2008; Zoheir and Lehmann, 2011). A spatial and genetic relationship has been observed between carbonatized ultramafics, subsequent granite intrusions and gold mineralization. Apparently carbonatization

preconcentrates gold up to 1000 times that of the original ultramafic rocks, and interaction with hydrothermal systems associated with granite intrusions may further concentrate gold (Cox and Singer, 1986). Listwaenites are considered a prime target for gold prospecting around Arabian-Nubian Shield ophiolites (Botros, 2004; Ahmed and Hariri, 2008; Zoheir and Lehmann, 2011).
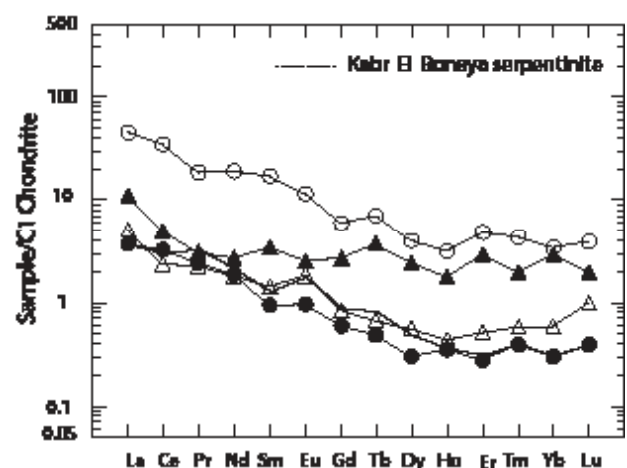

FIGURE 8 | Chondrite normalized REE plots for the averages of listwaenites and serpentinites. Chondrite normalization values are from Sun and McDonough (1989). Symbols as in Figure 6.

Mineralization associated with ophiolitic rocks in Egypt includes podiform chromites, talc, Cu-Ni-Co mineralization, magnesite and gold. Gold deposits are known to exist historically, associated with ophiolitic rocks, in the Wadi Allaqi region. Takla and Surour (1996) suggested that the serpentinized ultramafic rocks may have been an important source for gold. Botros (2004) suggested a genetic link between the vein-type mineralization hosted in sheared ophiolitic rocks in the Eastern Desert and the carbonatized-silicified serpentinite (listwaenite) along thrust zones. In the central Eastern Desert of Egypt, El-Sid gold mine is confined to hydrothermal quartz veins which occur at the contact between granite and serpentinite and extend into the serpentinite through a thick zone of graphite schist (El-Bouseily et al., 1985; Betros, 2004).

In the central and southern parts of the Eastern Desert of Egypt, listwaenite is commonly associated with ophiolitic serpentinites. The ore perspective of the listwaenites in the Eastern Desert of Egypt still remains unclear; although they are gold-bearing in many occurrences (e.g., Botros, 1993, 2002, 2004; Osman, 1995; Hassaan et al., 1996, 2009; Oweiss et al., 2001; Ramadan, 2002; Ramadan et al., 2005; Azer, 2008; Zoheir and Lehmann, 2011). The present data indicate that the gold content in listwaenites varies widely both among and within occurrences. These variations depend on lots of factors, including the presence of shearing, P-T conditions, reactions with host rocks, and the composition of the hydrothermal fluids. Some listwaenitic samples from the studied areas have Au grains and association of pyrite, chalcopyrite, cobaltite, covellite, goethite and malachite.

Petrogenesis

A variety of petrogenetic models have been proposed for the formation of listwaenite (e.g., Stanger, 1985; Kerrich, 1989; Auclair et al., 1993; Halls and Zhao, 1995; Uçurum and Larson, 1999; Uçurum, 2000; Hansen et al., 2005; Robinson et al., 2005; Akbulut et al., 2006; Santti et al., 2006; Nasir et al., 2007). Listwaenites are commonly associated with ophiolites and their formation is commonly attributed to carbonatization and silicification of ultramafic rocks. They can occur in two distinct geotectonic environments; subsequently to the obduction of the ophiolite into the continental crust (Ash, 2001), and in an oceanic environment during a pre- or syn-obduction process (Kishida and Kerrich, 1987; Buisson and Leblanc, 1987; Auclair et al., 1993; Tsikouras et al., 2006; Plissart and Femenias, 2009). The occurrence of relict chromite, fuchsite and high chromium and nickel contents in listwaenites of Wadi Allaqi area indicate an ultramafic protolith (e.g., Grapes and Palmer, 1996; Briga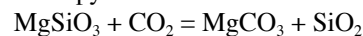tti et al., 2001; Nasir et al., 2007). Therefore, the present listwaenites are derived from a peridotite or its serpentinized equivalent. Also, the present listwaenites overprint the texture of the serpentinites indicating that listwaenite formed after emplacement of ophiolitic rocks.

The two studied types of listwaenites represent different stages of hydrothermal alteration. The large variations in their mineralogical and geochemical characteristics are due to the various different influence of reactions between the hydrothermal solutions and the protoliths which lead to different stages of metasomatic replacement. The hydrothermal fluids involved in the formation of carbonate-rich listwaenite were enriched in Ca, Mg, and CO_2, whereas those involved in the formation of silica-rich listwaenite were enriched in SiO_2. Hydrothermal solutions can permeate and alter the serpentinized peridotite trough the faults which cause fracturing of the serpentinites. Precipitation and recrystallization of carbonate and/or silica will form listwaenites depending on the amount of carbonate and silica and the pH of the solutions (Barnes et al., 1973). Serpentinized ultramafic rock acts as a sink for carbon dioxide from the migrating hydrothermal fluid. Carbonatization is represented by both the pervasive alteration and replacement of ultramafic rock by carbonate minerals. Carbonate minerals which replace the ultramafic rocks form by hydrolysis of iron, magnesium, calcium and manganese silicates to carbonates (Kishida and Kerrich, 1987; Kerrich, 1989). Carbonates take cations (Mg, Ca and Fe) but expel Si from ultramafic rocks according to the following reactions:
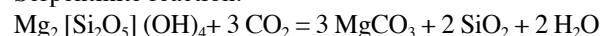
Olivine reaction:
$$Mg_2SiO_4 + 2CO_2 = 2MgCO_3 + SiO_2$$
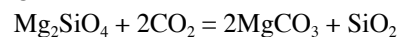
Orthopyroxene reaction:
$$MgSiO_3 + CO_2 = MgCO_3 + SiO_2$$

Serpentinite reaction:
$$Mg_2[Si_2O_5](OH)_4 + 3CO_2 = 3MgCO_3 + 2SiO_2 + 2H_2O$$

Fe is also liberated by carbonation of olivine and orthopyroxene.

The present data indicate that the listwaenites of Wadi Allaqi area formed by alteration of ultramafic rocks (especially serpentinites) and are commonly located within or near major faults and shear zones. With the circulation of hydrothermal fluids, primary ferromagnesian silicates of host rocks are replaced by Mg-Fe (-Ca) carbonates. Silica was dissolved from serpentinized peridotite into the hydrothermal fluids during the formation of carbonate-rich listwaenite because silica is more soluble at high pH, while the solubility of Ca increases with decreasing temperature at low partial pressure of CO_2 (Faure, 1991; Uçurum, 2000). The released silica forms quartz; and with the addition of potassium via the hydrothermal fluid it forms fuchsite.

The occurrence of fuchsite in the silica-rich listwaenite results from inherited Cr from the ultramafic host rock as it cannot be taken up by the carbonate (Boyle, 1979) and the addition of K+ from the circulation of hydrothermal fluids. The reactions of hydrothermal fluids with the ultramafic protolith to produce the listwaenite will also liberate a lot of trace elements – like gold – which originally resided in the source rocks.

The granitic intrusions may further concentrate gold in the listwaenites and facilitate the generation of mineralizing fluids. In this study, the presence of high Au, Ag, As, Ba, Sb, Zn, Cu and Pb contents reflects the polymetallic character of the listwaenites. Therefore, granitic intrusions can play a role in the concentration of some elements in the studied listwaenites because there are some silica-rich listwaenites around granodiorite intrusions. This suggests that there are two types of alteration in the serpentinized peridotite of Wadi Allaqi area. The first type may have taken place either whilst the ophiolite was part of the oceanic lithosphere or during its detachment from it. The second type of alteration is related to the migration of hydrothermal fluids through the rocks during the granitic intrusions.

CONCLUSIONS

Neoproterozoic rocks cropping out in the studied areas are part of the Allaqi-Heiani-Gerf suture, comprising allochtonous ophiolitic rocks, island arc assemblages, and syn-orogenic intrusions. The present study revealed that several mineralized and non-mineralized listwaenitic occurrences are scattered within the serpentinized ultramafic rocks in Wadi Allaqi area. Listwaenites are commonly located within or near major faults and shear zones. The composition differences in the studied listwaenites suggest differences in alteration intensity or composition of the protolith and/or chemistry of the hydrothermal fluids involved in their formation. Two types of listwaenites are recorded in serpentinite host rocks of Wadi Allaqi area; namely the silica-rich listwaenite and carbonate-rich listwaenite. Silica-rich listwaenite is recorded only in Jabal Shilman area adjacent to the granodiorite intrusion. It is composed of quartz (>40% of the rock) and carbonates together with smaller amounts of fuchsite and opaque minerals as well as minor antigorite, kaolinite, chromite and talc. The carbonate-rich listwaenite is composed mainly of carbonates (>60% of the rock) with variable amounts of quartz, kaolinite, antigorite, talc, and minor opaque minerals. The presence of fuchsite in the silica-rich listwaenite indicates that it is typical listwaenite, while the absence of the fuchsite in the carbonate-rich listwaenite indicates listwaenite-like rock. The silica-rich listwaenite is mineralized and enriched in precious metals, while the carbonate-rich listwaenite is non-mineralized.

The ore minerals accompanying the silica-rich listwaenite are represented mainly by gold, pyrite, chalcopyrite, cobaltite, covellite, goethite and malachite.

The present study indicates that gold content in the listwaenites increases in relation to the SiO_2 content. Also, there is a positive correlation between Au and some chalcophile trace elements (Ag, As, Sb, Cu, Zn and Pb), which suggests that these elements can be used as indicators of gold mineralization. Au values of the studied listwaenites are 400-1100 times enriched in comparison with those of the serpentinized peridotites. On this stage of investigations of the listwaenites in the Wadi Allaqi area, it is very difficult to give the entire evaluation for their metallogenic importance, but listwaenites are likely to be one of the most promising target for gold exploration in the future. Efforts must be concentrated on the exploration for new mineral deposits in the serpentinized segments of the ophiolitic belts in Egypt. Also, stable and radiogenic isotopic analyses of minerals associated with the listwaenites of Wadi Allaqi area are required to indicate the source of the mineralization fluids.

ACKNOWLEDGMENTS

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