

# Petrological characteristics of the mantle section in the Proterozoic ophiolites from the Pan-African belt

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### Abstract

Two Mid-Neoproterozoic ( $781 \pm 47$  Ma) ophiolites in the NE and NW Africa, Wadi Fiqo ophiolite, SED, Egypt and Bou-Azzer ophiolite, Anti-Atlas, Morocco, respectively, have been investigated. They are in various stages of dismemberment and severe alteration. But, almost all of the diagnostic ophiolite components can be found; namely, harzburgite tectonites, cumulate ultramafics, layered; although locally, and isotropic gabbros, plagiogranites, sheeted dykes and pillow lavas. Chromian spinel has been used as the only reliable petrogenetic indicator. Spinel from both Wadi Fiqo and Bou-Azzer ophiolites show high Cr# and low-Ti characters, indicating a high degree of partial melting in a sub-arc setting. The most striking difference between the two Neoproterozoic ophiolites, Wadi Fiqo and Bou-Azzer, is the pervasive CO<sub>2</sub>-metasomatism in the former. Field, petrographical and geochemical studies on the Bou-Azzer chromitites revealed that they are similar to the Phanerozoic equivalents.

Low-TiO<sub>2</sub> vein like magnetite deposits are present in the mantle section of Bou Azzer ophiolite. Two types of magnetite veins, I and II, can be recognized. The Type II magnetites sometimes include Co, Zn and Mn-rich chromian spinel in. We believe that Fe, Mn, Zn and Co were supplied from olivine upon serpentinization which accompanied the obduction of the Bou-Azzer complex.

## **1. Introduction**

### **1.1. Mantle composition and influence of partial melting**

The Earth's mantle is believed to consist of a heterogeneous assortment of ultramafic rocks, ranging in composition from fertile to depleted, lherzolite to dunite, respectively, passing through harzburgite. Plagioclase, spinel and/or garnet are the accessory minerals in the mantle defining stability fields with respect to pressure and temperature. At up to ~50 km depth, plagioclase becomes un-stable and reacts to form spinel in lherzolitic compositions. Spinel remains stable at depths up to ~80 km, when depth exceeds 80 km spinel reacts to form garnet in lherzolites. Garnet remains stable at up to ~400 km depth (e.g. Winter, 2001). All of these transitions occur as solid-state changes, and therefore do not affect the overall composition of the mantle (e.g. Winter, 2001).

The primary (fertile) mantle is subjected to depletion as a result of partial melting events which form primary melts in a variety of magmatic environments such as mid-ocean ridges and volcanic island arcs. These magmas rise through the mantle and the crust due to either mantle convection or density contrast, and leave behind residual or depleted mantle harzburgite (e.g. Jaques and Green, 1980; Takahashi and Kushiro, 1983; Winter, 2001). Successive episodes of partial melting can further deplete the residual mantle and alter the composition to highly depleted harzburgite then to pure dunite. Origin of dunite patches and veins has been controversial. A variety of origins have been proposed: residual (e.g. Moores and Vine, 1971); cumulative (e.g. Malpas, 1978); and/or replacive (e.g. Quick, 1981; Kelemen, 1990; Kelemen et al., 1995; Allan and Dick, 1996; Arai and Matsukage, 1996).

The shallowest part of the mantle is often subjected to larger degrees of partial melting, due to pressure decreasing and presence of H<sub>2</sub>O (e.g. Kushiro, 1969; Jaques and Green, 1980). Consequently, the upper mantle is the most likely site for the formation of dunites and chromitites (e.g. Quick, 1981; Arai and Yurimoto, 1995; Kelemen et al., 1995).

## 1.2. Spinel as petrogenetic and geotectonic indicator: An implication

As far as is well known, chromian spinel is a nearly ubiquitous accessory mineral in the mantle to crustal ultramafic rocks (e.g. Arai, 1992). The large proportion of the spinel group members are of high-temperature origin (e.g. King, 2004). The principal members of the spinel group have the formula  $AB_2O_4$ , where A is divalent cations such as  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$  and/or  $Co^{2+}$  and B is trivalent cations such as  $Cr^{3+}$ ,  $Al^{3+}$  and/or  $Fe^{3+}$ . Spinel group can be subdivided into three main series, according to the dominant B cation (e.g. Deer et al., 1992). (1) Spinel series (*sensu stricto*) with  $Al^{3+}$ ; (2) Magnetite series with  $Fe^{3+}$ ; and (3) Chromite series with  $Cr^{3+}$ . Extensive cation exchanges (solid solutions) have been observed between the members of each series (e.g. King, 2004; the present study).

Spinel structure based on the  $AB_2O_4$  formula, consists of an approximately cubic, close packing array of oxygen atoms in a layered arrangement perpendicular to the triad axis. Interstitial in this oxygen framework there are possible 32 octahedral and 64 tetrahedral coordination polyhedra of cations. Sixteen octahedral sites and eight tetrahedral sites are occupied by trivalent cations (B) and divalent cations (A), respectively (e.g. King, 2004). Consequently, the spinel structure can accommodate many elements and intermediate compositions have been occurred.

Furthermore, spinel can be classified normal (e.g. Spinel and Chromite series) or inverse (e.g. jacobsite in Magnetite series) (e.g. Deer et al., 1992), according to the position of cations in the above mentioned two sites. If the greater abundance of cations occurs in the octahedral site the spinel will be classified as normal ones. On the other hand, if the cations are equally divided between octahedral and tetrahedral sites such spinels will be classified as inverse ones.

Spinel is relatively resistant to natural chemical and physical attacks, but their alteration to ferritchromite, magnetite, chlorite, hydrotalcite, pyroaurite and stichtite is not uncommon (e.g. Bliss and MacLean, 1975; Burkhard, 1993; Ashwal and Cairncross, 1997). By contrast, spinels have been found as pseudomorphs after corundum, particularly in the presence of

the paragenesis phlogopite–corundum (e.g. Deer et al., 1992). The present study provides an example of extensive solid solution of spinels.

Chromian spinel has been used successfully as geotectonic and petrogenetic indicator in ultramafic to mafic rocks (e.g. Irvine, 1965, 1967; Dick and Bullen, 1984; Arai, 1992, 1994). Spinel compositions are so sensitive to changes in temperature, pressure, oxygen fugacity, bulk rock and fluid composition (e.g. Irvine, 1965, 1967). For the upper-mantle derived peridotites, the spinel compositions may indicate the degree of partial melting and have been used as a geotectonic indicator (e.g. Dick and Bullen, 1984; Arai, 1994). Chromian spinels sometimes memorize equilibrium temperatures in olivine-bearing rocks (e.g. Irvine, 1965, 1967; Jackson, 1969; Evans and Frost, 1975; Fabries, 1979). They have been used as a speedometer to show the cooling rate of olivine-bearing rocks (e.g. Ozawa, 1985). Moreover, it can be used as stress indicator (e.g. Ozawa, 1989), and oxygen barometer (e.g. Mattioli and Wood, 1986; Wood and Virgo, 1989) in peridotites and related rocks.

### **1.3. Metamorphism of ultramafic rocks**

Ultramafic rocks are metamorphosed at the ocean floor or within the crust during and after tectonic emplacement. Hydration of peridotites is known as serpentinization, which is considered the most famous metamorphic event affecting peridotites. Serpentinization process is a continuous process (e.g. O'Hanly, 1996). Clinopyroxene is more resistant than orthopyroxene and olivine, in descending order of resistance, against serpentinization.

Serpentinization reactions can be understood by (1) analysis of vent fluids from peridotite-hosted hydrothermal systems (e.g. Douville et al., 2002), (2) experimental and theoretical considerations (e.g. Allen and Seyfried, 2003) and (3) petrographic studies (e.g. Evans, 1977; Mével, 2003). Experimental studies have demonstrated that pyroxenes react faster than olivine at temperature above 250–300° C, but olivine reacts faster than pyroxene at temperature <250° C (e.g. Martin and Fyfe, 1970; Janecky and Seyfried, 1986; Allen and Seyfried, 2003). Serpentinization can be isochemical (constant chemistry) or allochemical (constant volume) process. The former is always

associated by volume increase, which causes fracturing or expansion fissure. In the latter, however, the  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Ca^{2+}$  and  $Si^{2+}$  ions-bearing serpentinizing-fluids are transported away from the system.

Upon metamorphism the reverse, i.e. dehydration of serpentinites, can occur and olivine is produced again (e.g. Arai, 1975; Evans, 1977; Nozaka, 2003). Such olivine is known as metamorphic olivine. By contrast, the primary olivine, which experienced the upper mantle ductile deformation, exhibits undulatory extinction and/or chemical zonation (e.g. Mercier and Nicolas, 1975).

What about the effect of  $CO_2$  instead of  $H_2O$ ? Johannes (1969, 1970) experimentally investigated equilibrium reactions in the system  $MgO-SiO_2-H_2O-CO_2$  at low and relatively moderate total pressures, 2 and up to 10 kbar. From our point of view, his work is considered a benchmark for the studies of carbonate-bearing metaperidotites and their phase relations and P-T- $X_{CO_2}$  conditions. One of Johannes's (1969) important conclusions is that serpentine can coexist only with a  $CO_2$ -poor fluid phase.

#### 1.4. What is an OPHIOLITE?

Historically the term "ophiolite" was derived from the Greek root "*ophio*" meaning snake or serpent. It was used by some authors, among other terms such as "*greenstones*", "*serpentinites*", "*roches vertes*", "*verdantique*", "*ophite*", and "*ophiocalcite*", to refer to altered ultrabasic and/or basic rocks which are usually associated with folded mountain belts and, therefore, deformed and metamorphosed during orogenic processes.

The term "ophiolite" refers to a distinctive rock association (e.g. Coleman, 1977), and was first introduced into the literature by Brongniart in 1813 in his "*Essai d'une classification mineralogique des roches mélanges*" (cited in Amstutz, 1979). In 1821, Brongniart published the first monograph on an ophiolite belt in the Apennines. He described a fourfold rock association consisting of (1) ultrabasics, (2) gabbros, (3) diabases-spilites, and (4) chert. He showed the textural, petrological and tectonic properties that were again mentioned one hundred years later by Steinmann (1927). In fact, Brongniart's

definition of the term ophiolite or ophiolite association is still valid and useful, because he included chert as an integral part of the ophiolite association. Whereas, Steinmann (1927) excluded in his famous "Steinmann's trinity" the "radiolarites" explicitly as "older rocks" emplaced by ophiolites (Coleman, 1977).

In 1972, subsequent to the near-universal acceptance of plate tectonics, the Penrose Conference of the Geological Society of America on ophiolites redefined ophiolite as an assemblage of basic and ultrabasic rocks with a specific composition and stratigraphy (Coleman, 1977) (Fig. 1).

The Penrose Conference dealing with ophiolite did not include *mélanges* in its terminology. *Mélanges* are simply considered to be the result of severe tectonism along convergent plate margins (e.g. Coleman, 1977).

*Mélanges* are tectonically chaotic rock units that are most important products of plate collision. There are two types of *mélange*, tectonic and sedimentary (or olistostrome). Both types of *mélange* are found on the outer-side of the trench-arc gap near the landward side of the trench, and both are related to the under-thrusting tectonics at convergent plate margins. They incorporate blocks of ophiolites from a mid-oceanic ridge or from mid-extensional zones of marginal or rear arc basins. Gansser (1974) suggested the term "ophiolitic *mélange*" which is defined as an olistostromal and tectonic mixture of ophiolitic materials and oceanic sediments with exotic blocks, reflecting areas which have disappeared. Furthermore, Gansser (1974) explained the formation of this *mélange* through a mechanism related to obduction of oceanic crust. Ophiolite studies have been a key for understanding of the mantle, the formation and genesis of oceanic crust, and the nature of collisional tectonic events.

Two fundamental questions concern ophiolite complexes world-wide. (1) What is their original tectonic setting (MOR, transform fault or SSZ)? (2) How were this dense oceanic lithosphere emplaced onto the more buoyant, less-dense continental crust? (Searle and Cox, 1999).

The internal structure of the ophiolite sequence depending mainly on which part of the section has been exposed and how was the succession

emplaced. The observed metamorphic facieses within ophiolite sequences range from blue schist or high-grade granulite to lower green schist facies or minimal metamorphism. In a complete ophiolite section (e.g. Semail ophiolite, Oman) (Fig. 1), the expected obduction front will be the mantle section which is overlain by MTZ dunites. The latter grading upward to layered gabbros, massive gabbros, diorites and plagiogranites. Sheeted dykes overlie the plagiogranites and in turn are overlain by a layer of mafic extrusive rocks, mostly pillow and/or massive basalts. The uppermost layer of a typical ophiolite complex is composed of deep sea sediments (e.g. Leblanc, 1981; Searle and Cox, 1999; Kusky, 2004).

It is believed that the group of rocks overlying the harzburgite tectonite was crystallized from magmas produced by partial melting of some peridotite more fertile than this harzburgite (e.g. Kusky, 2004). The crust-mantle boundary (Moho transition zone) is not straightforward. Moreover, Moho transition zone sharing characters with mantle and crust (e.g. Nicolas and Prinzhofer, 1983). It is essentially dunitic, and contains wehrlites, pyroxenites, troctolites and chromitites.

### **1.5. Proterozoic ophiolites: General Remarks**

The Pan-African orogenic belts (Fig. 2) extend from northwest Africa (e.g. Anti-Atlas belt) to the Arabian Nubian Shield (ANS), east Africa, Middle East and southward to Brazil, and also they occur in North America and Europe (e.g. Schenk, 1971; Rast and Skehan, 1983; Nance et al., 1991; Kröner, 1993; Rogers et al., 1995; Trompette, 1997; Hefferan et al., 2000). The orogenic belts appear to have developed as a result of successive collisions of magmatic arcs, mélanges and amalgamated terranes with rifted continental margins (e.g. Black et al., 1994). Hence, they could display remarkably similar histories of allochthonous terranes, calc-alkaline intrusions, metamorphism, ophiolite emplacement, mélange generation and molasse deposition (e.g. Hefferan et al., 2000). The term *Pan-African Event* was originally proposed by Kennedy (1964) to denote a tectono-magmatic episode (prevailing at the Late Proterozoic to the end of Precambrian) that caused



remobilization, deformation, migmatization and anatexis of the Archean and Proterozoic rocks, and large-scale intrusion of granites (e.g. Hassan and Hashad, 1991). Gass (1981) used the term to describe the whole process of cratonization of oceanic arc complexes and their collision and welding to the older African Craton.

As far as is well-known the Late Proterozoic Arabian Nubian Shield (ANS) (the massive graveyard of Neoproterozoic oceanic lithosphere) hosts a number of ophiolite-decorated sutures, and boasts one of the highest ophiolite densities ever known for a Proterozoic terrane on the earth (e.g. Kusky, 2004; Stern et al., 2004).

The ANS is the largest tract of juvenile continental crust of Neoproterozoic age on Earth (Patchett and Chase, 2002). The ANS is part of the East African Orogen that has a complex history including a record of the break-up of Rodinia at circa 900–800 Ma, and the evolution of numerous arc systems, oceanic plateaux, oceanic crust and sedimentary basins (e.g. Stern, 1994; Stein and Goldstein, 1996; Kusky et al., 2003; Kusky, 2004). The Neoproterozoic closure of the Mozambique Ocean resulted in a complex amalgam of arc, ophiolite and micro-continental terranes, the Arabian Nubian Shield (ANS) (e.g. Kusky et al., 2002). The ANS was subsequently overburied by the Phanerozoic sediments; in the Oligocene and younger times the ANS has been exposed by uplift and erosion on the Red Sea flanks (Stern et al., 2004).

The Neoproterozoic (< 1000 Ma) ophiolites are more abundant than the Paleo- (1650–2300 Ma) and Meso- (1000–1400 Ma) Proterozoic ones (Kusky, 2004). A few Mesoproterozoic ophiolites have been described from the Karelian Shield, Cape Smith Belt, West Africa, and the southwest USA (e.g. St-Onge et al., 1989; Abouchami et al., 1990; Scott et al., 1992; Boher et al., 1992; Dann, 2004). According to our knowledge, Jormua ophiolite (Peltonen and Kontinen, 2004 and references therein) is one of the best striking examples for the Paleoproterozoic ophiolites.

The occurrence of ophiolites decorating suture zones and their association with calc-alkaline rocks of island arc affinities have led several authors (e.g. Bakor et al., 1976; Gass, 1981; Shackleton et al., 1980) to assume/propose an Upper Proterozoic plate-tectonic model for the evolution of the Pan-African

belts in the Arabian Nubian Shield. The latter proposal is extended to explain the evolution of the Pan-African belts in: Nigeria (McCurry, 1976; McCurry and Wright, 1977), Morocco (Leblanc, 1975, 1981, Saquaque et al., 1989) and Mali (Black et al., 1979).

The abundance of ophiolites within the Pan-African orogenic belts (ANS and those surrounding the West African Craton) is a further indication that their crust and lithosphere were produced by processes similar to those of the modern plate tectonics (e.g. Leblanc, 1981; Hefferan et al., 2000; Stern et al., 2004). Contrary to the Bou-Azzer ophiolite along the Moroccan Anti-Atlas suture, the orientation of ophiolite-decorated sutures within the ANS is difficult to be defined (e.g. Church, 1988; Stern et al., 1990). The ANS mafic-ultramafic complex is rather complicated; it shows sea floor spreading environments as well as some appear to be roots of island arcs (Darb Zubaydah in Arabia; Quick and Bosch, 1989), and others are autochthonous layered intrusions (Dahanib in Egypt; Dixon, 1981).

Serpentinite masses of the Egyptian Eastern Desert were first defined as ophiolites by Rittmann (1958), although the term *ophiolite* according to the definition of the GSA Penrose Conference (1972) have been firstly used by Bakor et al. (1976), Garson and Shalaby (1976) and Neary et al. (1976). According to our perusal, personal communications and field trips in ANS and Moroccan Anti-Atlas regions, the best preserved, to some extent complete, ophiolites are recorded in Table 1.

## **2. The current study**

### **2.1. Scope**

More information on the Proterozoic-age ophiolites is needed particularly since the suggestion of Wynne-Edwards, (1976) that there have been important changes in the conditions of crustal evolution since the upper Proterozoic.

This contribution is aimed at being an overview on the geology of Neoproterozoic ophiolites, mainly on petrological characteristics of the mantle section of two well-known Neoproterozoic age ophiolite suites, Wadi

Fiqo, SED, Egypt and Bou-Azzer, Anti-Atlas, Morocco. The main goal of this study can be achieved throughout:

(1) Defining the petrological characteristics and tectonic setting of the two ophiolitic mantle sections, Wadi Fiqo and Bou-Azzer, based on their petrographical and chromian spinel characteristics,

(2) Clarifying the origin of Bou-Azzer chromitites and their dunite envelope, and suggesting a plausible model for their genesis, and

(3) Comparing between the studied Neoproterozoic ophiolites and their Phanerozoic analogues to examine the change in the geothermal regime, if any, from the Neoproterozoic to Phanerozoic era.

One of the most striking characteristics of the Proterozoic ophiolites is their metamorphism to variable extents. Consequently, we intended to clarify the origin of Wadi Fiqo carbonate-orthopyroxenites, among other metaperidotites.

Bou-Azzer serpentinites exhibit a peculiar field for studying element mobility during serpentinization, which can be manifested in the development of magnetite veins (Gahlan et al., in press) and Co, Zn and Mn-rich chromian spinels (Gahlan and Arai, submitted).

Hence, we intended to specify the origin of two types, I and II, of magnetite veins in the Bou-Azzer serpentinites. Furthermore, we aim to establish the origin of Co-, Zn- and Mn-rich chromian spinel in peridotites during low-temperature metamorphism.

The above mentioned research could be accomplished throughout:

(1) Four field trips to the study areas with detailed field work by the aid of aerial photographs or previously made geological maps,

(2) Studying the structural contacts between the different rock units exposed throughout the investigated areas,

(3) Collecting representative samples from the rocks under investigation,

(4) Processing the collected rock samples into polished thin sections,

(5) Petrographical works on the thin sections to identify the rock-forming minerals, fabrics, textures and inclusions, if any, and

(6) Obtaining chemical characteristics of the studied rocks with XRF, EPMA and LA-ICP-MS, and buying bulk-rock PGE data from the Genalysis Laboratory Services, Australia.

## 2.2. Brief overview on the current study

Two Mid-Neoproterozoic ( $781 \pm 47$  Ma) ophiolites in the NE and NW Africa, Wadi Fiqo ophiolite, SED, Egypt and Bou-Azzer ophiolite, Anti-Atlas, Morocco, respectively, have been investigated (Figs. 3 & 4). They are in various stages of dismemberment and severe alteration. But, almost all of the diagnostic ophiolite components can be found; namely, harzburgite tectonites, cumulate ultramafics, layered, even locally, and isotropic gabbros, plagiogranites, sheeted dykes and pillow lavas. They mark suture zones, which indicate fossil subduction zone locations. Broadly, they were emplaced while still hot enough to metamorphose the underlying continental marginal rocks. Some discrimination diagrams grossly indicate a fore-arc tectonic setting modification; i.e. they were located at the hanging-wall of convergent plate margins.

Wadi Fiqo mafic-ultramafic fragments represent a thrust sheet of folded ophiolitic *mélange* pertaining to the Mid-Neoproterozoic Pan-African belt of the South Eastern Desert of Egypt and northeast Sudan. The ultramafic section in the studied area is mostly characterized by a complex serpentinite-metaperidotite amalgam of harzburgite-dunite parentage. Almost all the primary silicates have been metamorphosed-out except chromian spinel. The latter has been used as the only reliable petrogenetic and geotectonic indicator. The almost complete absence of clinopyroxene in the peridotites combined with the high Cr# (0.6–0.9) (Fig. 5) and low-Ti character of the intact chromian spinel indicate a high degree of partial melting in a fore-arc setting. Hence, the protolith of Wadi Fiqo meta-ultramafics is estimated to be a highly depleted residual peridotite with at least 25 % of partial melting.

The original mantle peridotites have been metamorphosed regionally from greenschist to amphibolite facies. CO<sub>2</sub>-metasomatism associated with the amphibolite facies metamorphism resulted in the formation of various carbonate-bearing meta-ultramafics, such as carbonate-orthopyroxenites. The latter are reported for the first time from the Late Proterozoic Pan-African ophiolites of the Arabian Nubian Shield. The country rocks to the carbonate-orthopyroxenites are mainly migmatized gneisses and mobilizates.

Metasomatic/metamorphic conditions of carbonate-orthopyroxenites are assumed to be consistent with those of the country rocks, i.e. at least 6 kbar, 630° C, high  $X_{\text{CO}_2}$  and water-deficiency.

The Mid-Neoproterozoic Bou-Azzer ophiolite offers a continuous sequence, particularly at Wadi Ait-Ahmane, from the mantle section below the mafic crust upward to the sedimentary cover overlying basalts. The Bou-Azzer mantle section is severely serpentinized and dominated by harzburgite with small dunite lenses. Small-scale concordant chromitite pods and discordant pyroxenite dykes are sparsely distributed in the mantle section. The late-stage wehrlitic intrusions have been observed in the crustal gabbro. Due to the severe serpentinization, almost all the primary silicates have been converted to the serpentine-magnetite assemblage. We were, however, able to identify the primary lithologies by the aid of relic textures and chromian spinel chemistry and morphology. In general, chromian spinel in both chromitites and associated peridotites exhibits a restricted compositional range, although it is more uniform in chemistry in the former than in the latter. Spinels are highly chromian ( $\text{Cr}\# = 0.75 \sim 0.87$ ) and highly magnesian ( $\text{Mg}\# = 0.57 \sim 0.74$ ) in chromitites (Fig. 5). Likewise, they are highly chromian ( $\text{Cr}\# = 0.6 \sim 0.7$ ) and moderately to highly magnesian ( $\text{Mg}\# = 0.2 \sim 0.5$ ) in the associated peridotites (Fig. 5). Furthermore, they are generally poor in Ti and  $\text{Fe}^{3+}$  both in the chromitites and in associated peridotites. These lines of evidence combined with the whole-rock depletion in  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and CaO, and enrichment in Ni relative to Co indicate that the Bou-Azzer upper mantle was highly refractory.

Given the above characteristics, the general petrological characteristics of the Mid-Neoproterozoic Bou-Azzer chromitites and associated peridotites are similar to those of the Phanerozoic ophiolites. Moreover, chromitite pods may have been formed by the same way as the Phanerozoic ones, namely by melt-peridotites interaction and subsequent melt mixing. The high  $\text{Cr}\#$  combined with the low-Ti character of spinel suggests the formation of Bou-Azzer ophiolite in a sub-arc environment.

Vein-like deposits of low- $\text{TiO}_2$  (<0.03 wt %) magnetite are present in the mantle section of Bou Azzer ophiolite. Two types of magnetite veins, I and II,

can be recognized: magnetite is fibrous in Type I, but is stout or idiomorphic in Type II (Fig. 6). Mode of occurrence and petrography indicate they had formed filling the open space of cracks. Magnetite is Ni-bearing in Type I, and is Ni-free and sometimes includes Mn-rich chromian spinel in Type II. Magnetite is commonly accompanied by serpentine and magnesite in Type I, and by chlorite (clinochlore), serpentine, talc and lesser amount of garnet (andradite) in Type II. *In-situ* trace-element analysis shows depletion with Al, Si, V, Cr and Zn in the vein magnetite relative to the disseminated one in wall serpentinite. Positive slope of PGE distribution pattern and Au enrichment were the result of hydrothermal activity. The formation of magnetite veins was apparently associated with enrichment of magnetite components in chromian spinels. The iron was supplied from olivine upon serpentinization which accompanied the obduction of the Bou-Azzer complex. The iron mobility may have been enhanced by high water/rock ratio of the serpentinization.

The peculiar Co, Zn and Mn-rich chromian spinels are hosted by magnetite veins, serpentinites and chromitites of the mantle section of the Mid-Neoproterozoic Bou-Azzer ophiolite. The spinels are complexly zoned either optically or chemically, and exhibit anomalously high MnO, ZnO and CoO contents (up to 22, 7.5 and 2 wt. %, respectively). They have four distinct optical zones, particularly in the magnetite veins and serpentinites. The highest level of these elements, probably divalent, is recorded within the ferritchromite zone and/or within the core zone if the ferritchromite zone is absent. These elements as well as Fe exhibit enrichment also along fractures of the altered spinels. Fe, Mn, Zn and Co were most probably supplied from olivine upon serpentinization, which have been prevalent during and after obduction of the ophiolite.

The enrichment of the Bou-Azzer chromian spinel in Mn, Zn and Co was governed mainly by the fluid/ mineral (spinel) ratio among other factors including metamorphic temperature, spinel fracture system and fluid accessibility. Co-, Zn- and Mn-rich chromian spinels can be used as an exploration guide for Co-Ni-Zn-Cu sulfide mineralization associated with serpentinized peridotites.

### **2.3. Concluding Remarks**

#### **Sub-conclusion (A) Petrological characteristics of Wadi Fiqo serpentinites and metaperidotites**

- (1) Field, petrography and mineral chemistry affirm that the different ophiolite occurrences (klippen) represent originally one major thrust sheet which later has been dissected by faults and separated into klippen.
- (2) The nearly complete absence of clinopyroxene combined with the general high Cr# and low-Ti character of chromian spinel indicate that: (a) highly depleted protolith and (b) sub-arc setting (fore-arc).
- (3) The formation of Cr-rich but low Fe<sup>3+</sup> spinels of the magnesite-bearing talc-forsterite schist was due to upper greenschist facies metamorphism at extremely low  $fO_2$  conditions.

#### **Sub-conclusion (B) Petrological characteristics of Bou-Azzer harzburgite, dunite and chromitite**

- (1) The whole rock chemistry of the serpentinitized harzburgites shows marked depletion in TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO, and enrichment in Ni relative to Co, reflecting the highly refractory nature of the protolith.
- (2) The high Cr# combined with low-Ti character of spinels suggests sub-arc tectonic setting for Bou-Azzer ophiolite.
- (3) The Neoproterozoic Bou-Azzer podiform chromitites may have been formed by the same way as the Phanerozoic equivalents, namely by melt-peridotites reaction and subsequent melt mixing.
- (4) It seems that the Bou-Azzer harzburgite was initially developed in a back-arc setting, and afterward has been modified in a fore-arc setting to produce boninitic magma (dunite/chromitite bodies) above a new subduction zone.
- (5) Stichtite formation is a low-temperature replacement process of altered chromian spinel without any recognizable effects on the relict spinel cores.

#### **Sub-conclusion (C) Critical comparative studies**

- (1) A considerable large similarity has been observed between the studied Proterozoic ophiolites and the Phanerozoic equivalents, suggesting that there

has been no considerable change in geothermal regime of the earth since the Late Proterozoic era.

(2) The Neoproterozoic Bou-Azzer chromitites are moderately lower in  $TiO_2$  than the Phanerozoic equivalents. By contrast, they have the same field relations with the host rocks; namely chromitite is enveloped by dunite and both are collectively enclosed by harzburgite screen.

(3) Phase relations indicate a striking difference between the fluid/rock ratio and reaction pathways between Wadi Fiqo and Bou-Azzer ophiolites.

#### **Sub-conclusion (D) Origin of Wadi Fiqo carbonate-orthopyroxenites and metamorphic evolution of the ultramafics**

(1) Regional and/or contact metamorphism accompanied by  $CO_2$ -metasomatism affected the Wadi Fiqo peridotitic ultramafic rocks and resulted in the formation of carbonate-orthopyroxenites.

(2) Carbonate-orthopyroxenites cannot exist at magmatic conditions.

(3) The estimated metamorphic conditions for the formation of carbonate-orthopyroxenites are at least  $630\text{ }^\circ\text{C}$ , 6 kbar (20–25 km depth), high- $X_{CO_2}$  and water-deficiency.

(4) The secondary orthopyroxene is characterized by very long prismatic habit, absence of chemical zonation and exsolution lamellae of Ca-rich pyroxene, extreme depletion in Ca, Al and Cr, and MREE enrichment.

(5) It is highly possible that the source of Wadi Fiqo metasomatising  $CO_2$ -rich fluids was the shelf sediments of the passive continental margin; the  $CO_2$ -rich fluids used shear zones as pathways to cause such metamorphism.

(6) The development of various carbonated metaperidotites was due to variable  $X_{CO_2}/H_2O$  ratios and temperatures during metamorphism.

#### **Sub-conclusion (E) Genesis of magnetite veins**

(1) The magnetite veins are found in serpentinized harzburgite of the Bou-Azzer ophiolite and are considered to be *epigenetic deposits* formed along with the serpentinization process during and after the obduction of the ophiolite complex.



(2) Magnetite is fibrous, Ni-rich and Cu-poor in Type I veins, and is stout or idiomorphic, Ni-poor, Cu-rich, and contains garnet (andradite) and Mn-rich chromian spinel in Type II veins.

(3) The hydrothermal solution for Type I magnetite veins was slightly different in chemistry from that for Type II.

(4) The source of iron was internal, supplied from olivine upon serpentinization. The mineralizing hydrothermal fluids utilized shears, cracks and tension joints for transportation and precipitation of iron, which was transported as ferrous hydroxide. The intensity of transportation and precipitation of iron was mainly governed by the fluid/ rock ratio, which apparently lower in Type I area than Type II area.

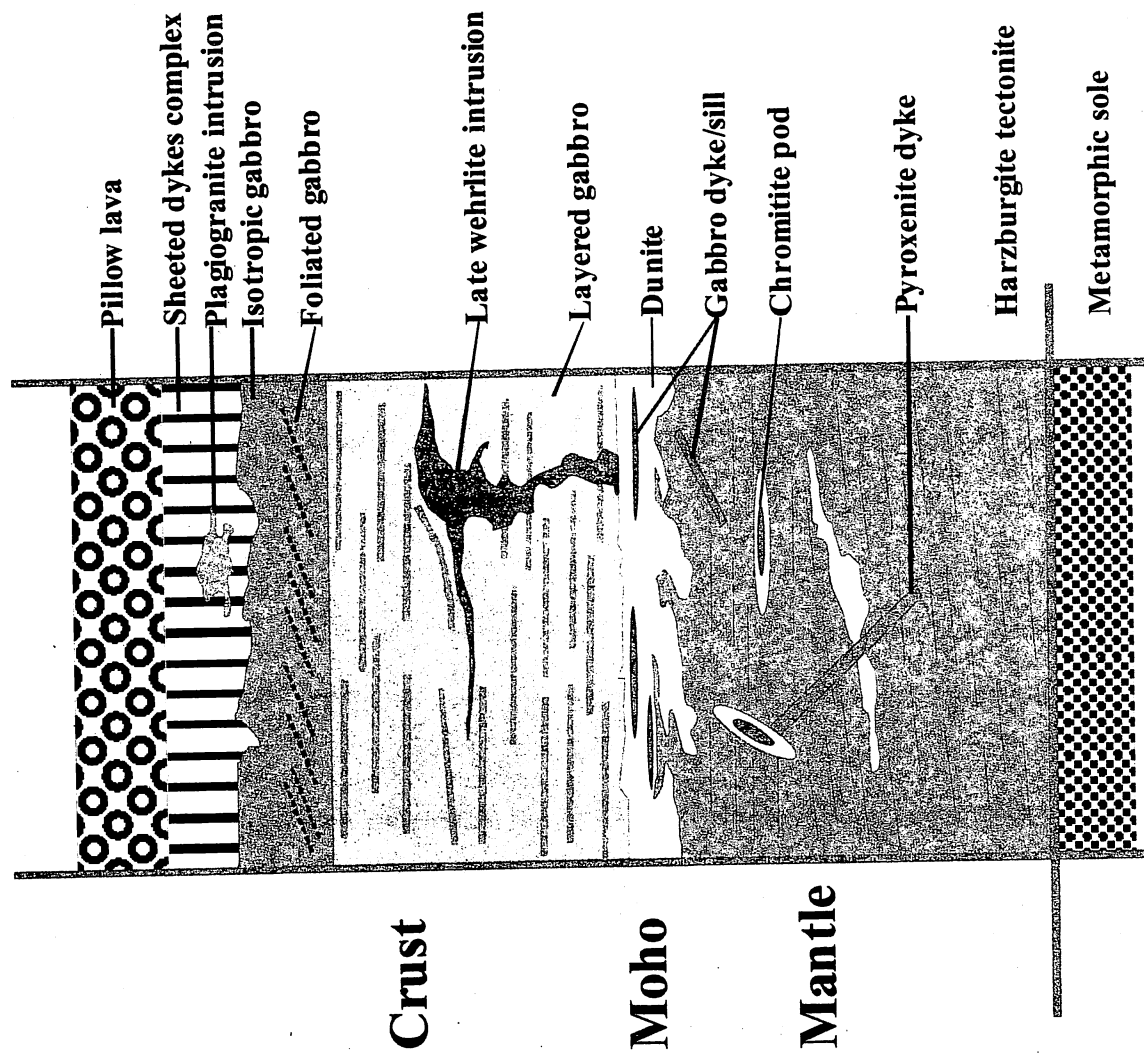
#### **Sub-conclusion (F) Genesis of Co, Zn and Mn-rich chromian spinel**

(1) We discovered and described for the first time a peculiarly zoned Mn ± Zn ± Co-rich chromian spinel in magnetite veins, serpentinites and chromitites (in the order of enrichment) from the Bou-Azzer mantle section. The Bou-Azzer chromian spinel shows a complex optical (up to four zones), cryptic and chemical zonation.

(2) The enrichment of Mn, Zn and Co in chromian spinel increases, on average, from chromitite through harzburgite to magnetite veins. Mn, Zn and Co have the same behavior and attain their highest concentrations along the chromian spinel grain boundaries and fractures, which played an important role as pathways for involved fluids.

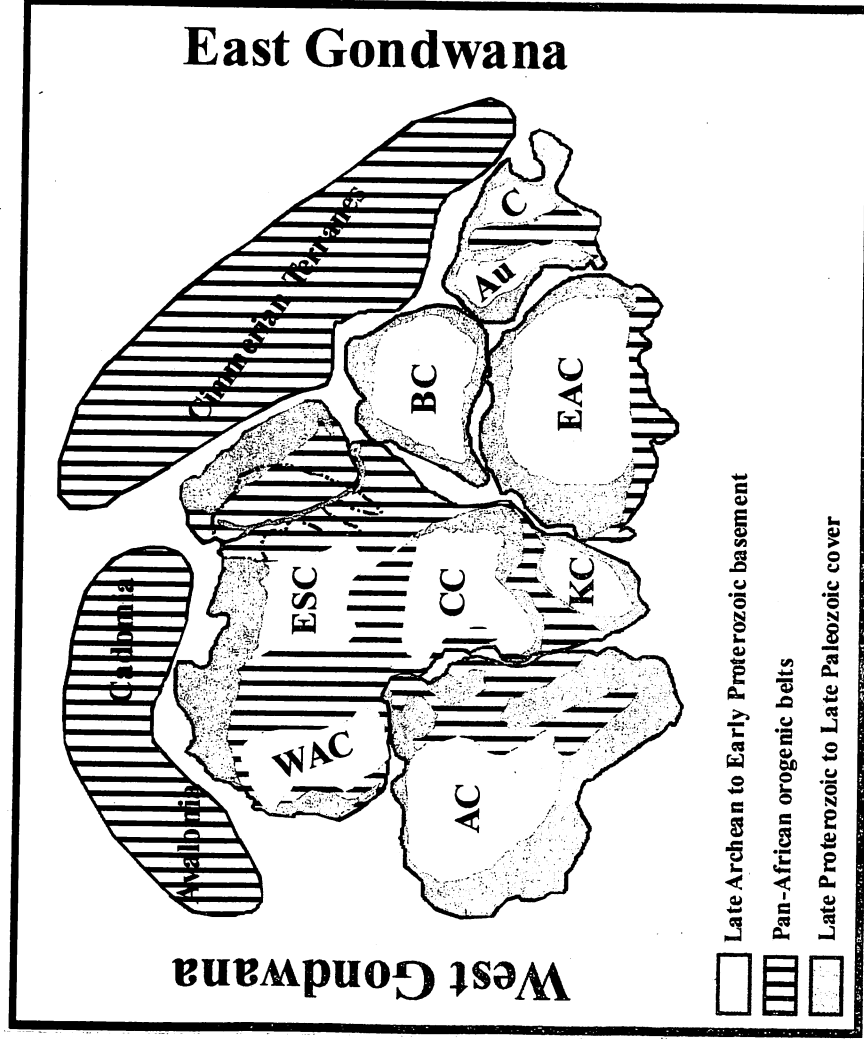
(3) The Mn, Zn and Co enrichment and the ferritchromite formation were governed mainly by fluid: spinel ratio among other factors.

(4) Co, Zn and Mn-rich spinels could manifest Co-Ni-Zn-Cu sulfide mineralization associated with serpentinites.



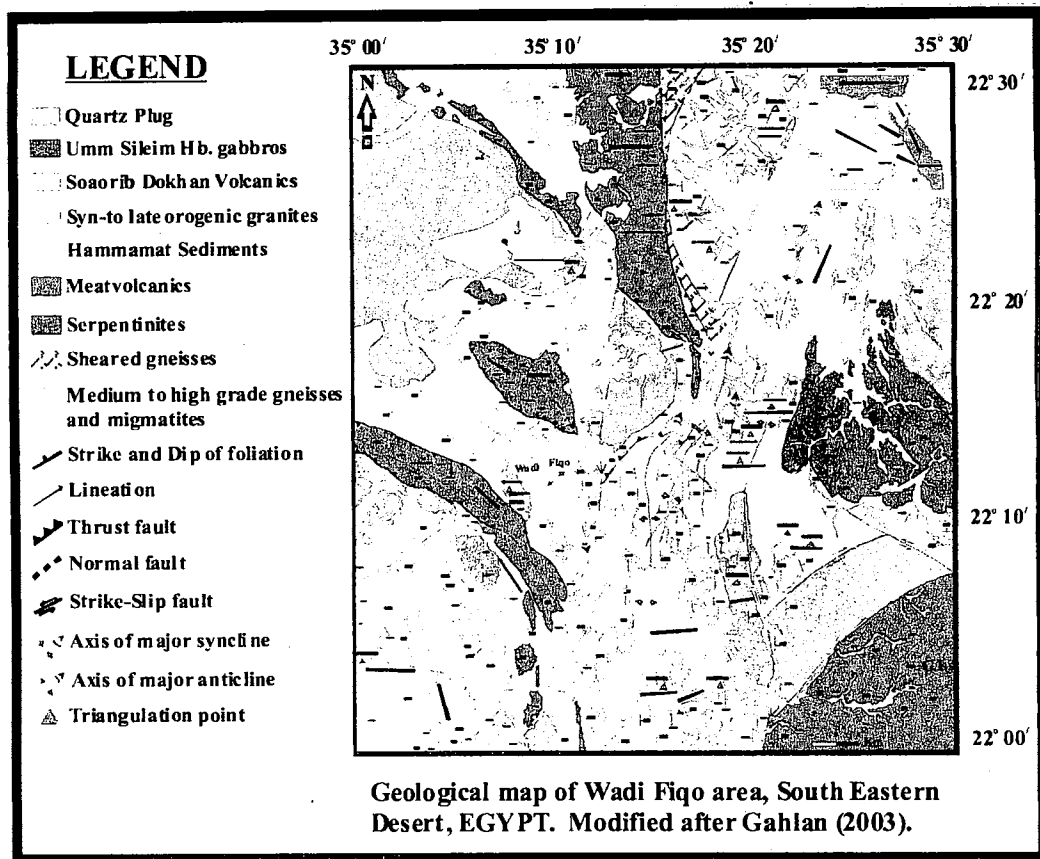
**Fig. 1**

An idealized ophiolite sequence shows the mantle section, Moho transition zone and crust, similar to the most famous Oman ophiolite succession (e.g. Nicolas, 1989).



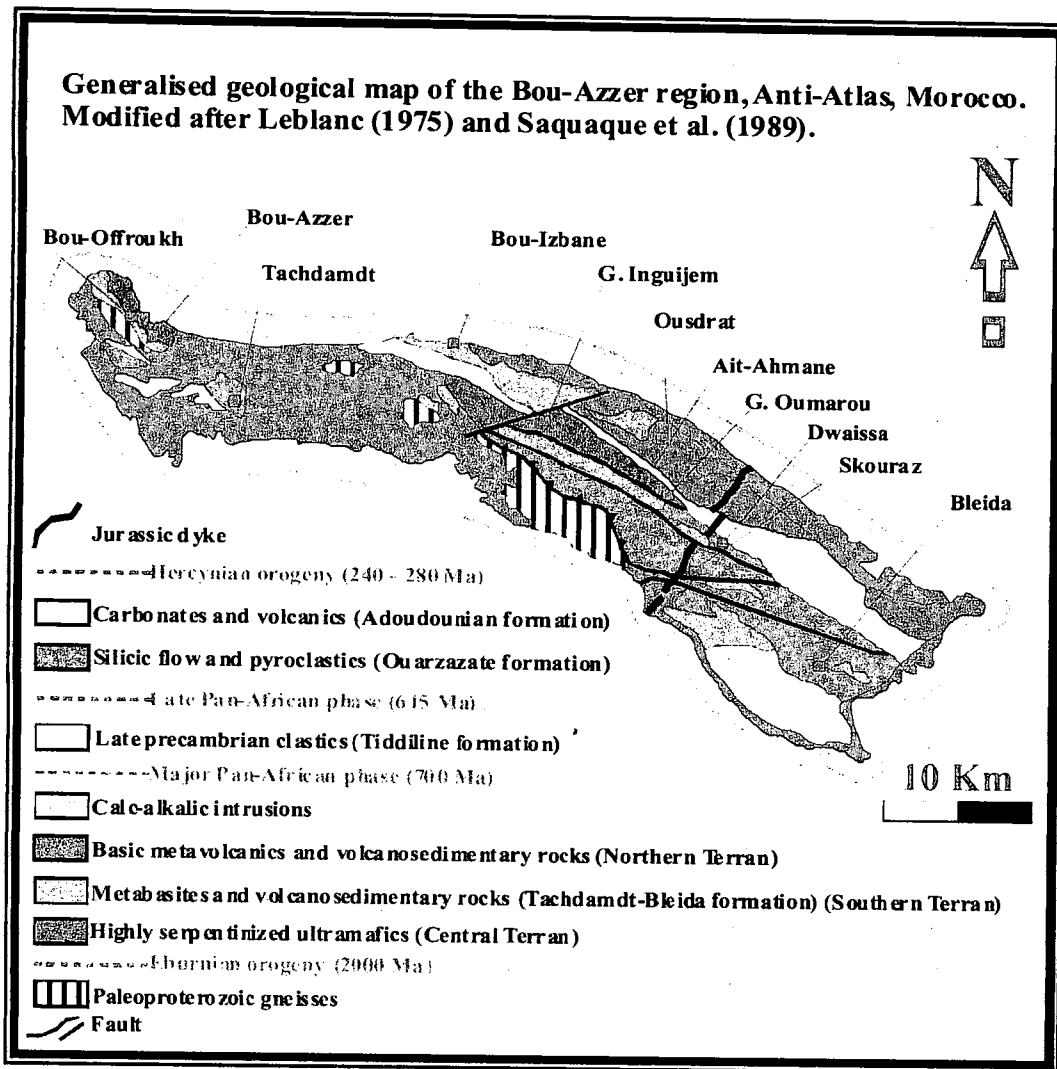
**Fig. 2**

Distribution of Pan-African orogenic belts enclosing older cratons, in the frame of the latest Neoproterozoic reconstruction of Gondwana by Unrug (1997) and modified by Hefferan et al. (2000). The dotted-dashed field encloses the volcanic arcs of the Arabian Nubian Shield. WAC West African Craton; ACAmazon Craton; ESCEast Saharan Craton; CCCongo Craton; KCKalahari Craton; BCBundel Khand Craton; EACEast Antarctic Craton; AuCAustralian Craton.



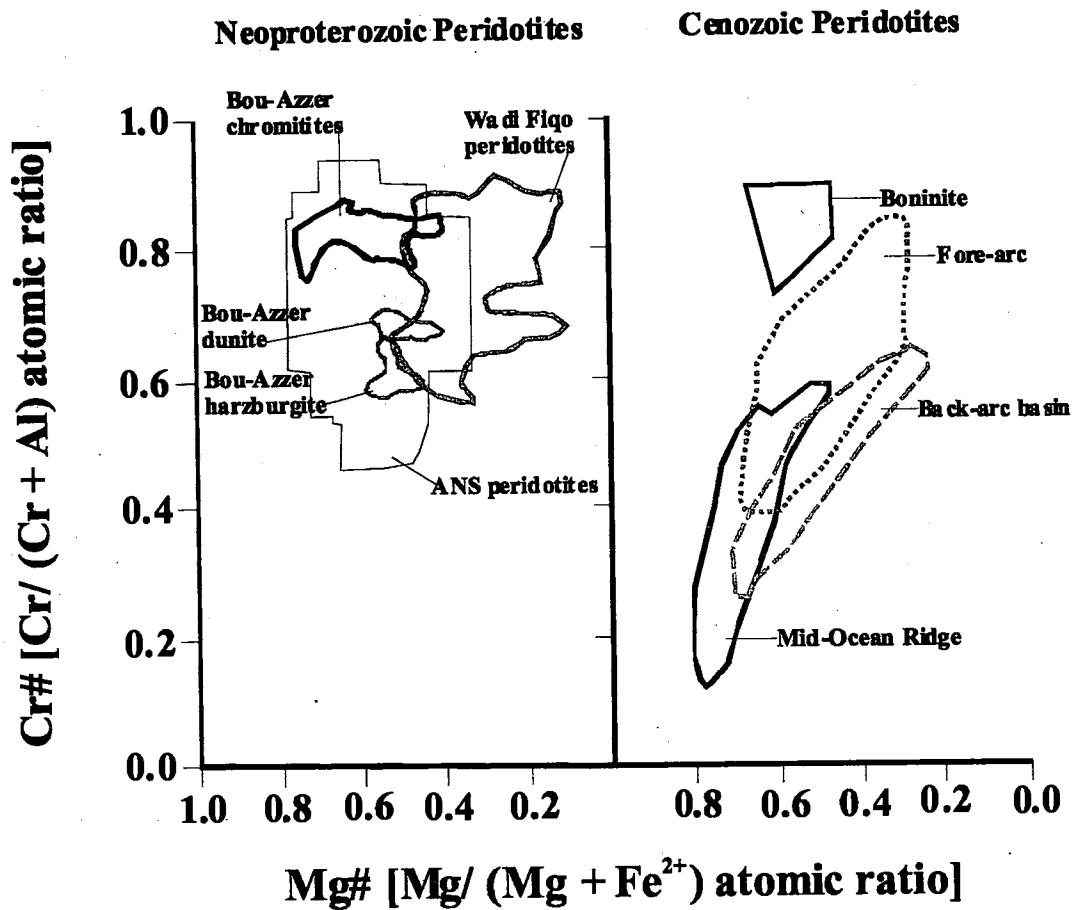
**Fig. 3**

Geological map of Wadi Fiqo area, South Eastern Desert Egypt (modified after Gahlan, 2003).



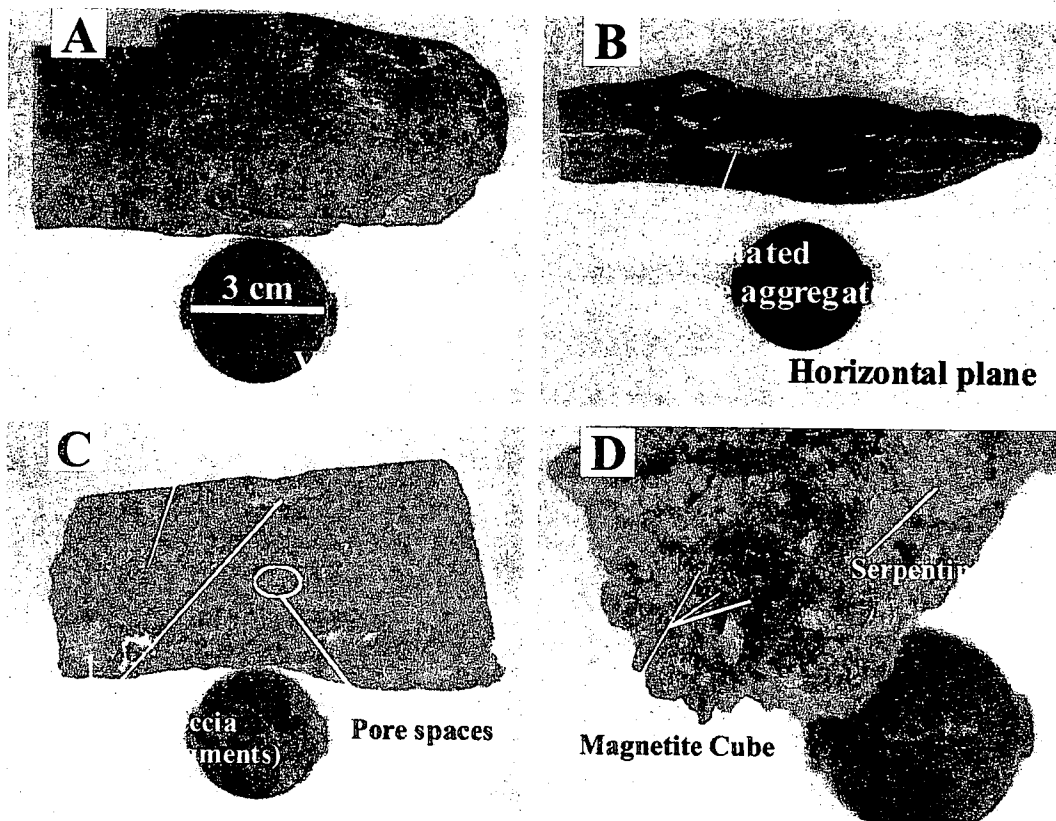
**Fig. 4**

Generalized geological map of the Bou-Azzer region, Anti-Atlas, Morocco.  
Modified after Leblanc (1975) and Saquaque et al. (1989a).



**Fig. 5**

A comparison, in the terms of spinel composition, between the Neoproterozoic Bou-Azzer and Wadi Fiqo ophiolites and the Cenozoic age analogous ophiolitic fields (Bloomer et al., 1995). The shaded field of the Neoproterozoic Arabian Nubian shield peridotites is after Stern et al. (2004). Note that the vast majority of the Bou-Azzer and Wadi Fiqo ophiolitic peridotites and the associated chromitites are plotted in the field of ANS peridotites; suggesting, overall, fore-arc setting.



**Fig. 6**

A. A wall of Type I magnetite vein. Note the clear fibrous texture. B. A slab of Type I magnetite vein. Perpendicular view to the wall, showing the S-c fabric as a result of dextral heterogeneous simple shear. Note the light green coprecipitated serpentine aggregates. C. A sawed surface of Type II magnetite vein showing a massive character. Note the light green serpentine wall-rock aggregates (breccia) and the millimeter-size pores. D. Close-up view of a pin-hole void covered with idiomorphic magnetite crystals in Type II vein.

**Table 2-1.** The best preserved Pan-African ophiolites in the ANS and Morocco

<b>Ophiolite Name</b>	<b>Country</b>	<b>Reference</b>
Bou-Azzer	Morocco	Leblanc (1976, 1981), Ahmed et al. (2005), Gahlan et al. (2006)
Darb Zubaydah	Saudi Arabia	Quick (1990)
Bi'r Tuluhah	Saudi Arabia	Pallister et al. (1988)
Wadi Khadra	Saudi Arabia	Quick (1991)
Halaban	Saudi Arabia	Al-Saleh et al. (1998)
Ess	Saudi Arabia	Pallister et al. (1988)
Al wask	Saudi Arabia	Bakor et al. (1976)
Tharwah	Saudi Arabia	Nassief et al. (1984)
Bi'r Umq	Saudi Arabia	Shanti (1983)
Tathlith	Saudi Arabia	Pallister et al. (1988)
Arbaat	Sudan	Abdelsalam and Stern (1993)
Sol-Hamed	Sudan	Fitches et al. (1983)
Wadi onib	Sudan	Hussein et al. (1983)
Sol-Hamed	Egypt	Nasr and Beniamin (2001), Gahlan (2003)
Gerf	Egypt	Zimmer et al. (1995), Nasr et al (1996), Gahlan (2003)
Wadi Ghadir	Egypt	El-Sharkawi and El-Bayoumi (1979) El-Bayoumi (1983), Khudeir (1983)
Fawakhir	Egypt	Nassief et al. (1980) El-Sayed et al. (1999)

<sup>a</sup> The table is modified after Stern et al. (2004) and the references are cited therein.



## 学位論文審査結果の要旨

ヒシャム・ガハラン君の提出論文および、平成18年8月4日の口頭発表の結果をもとに審査委員会を開催し、以下の結論を得た。ガハラン君は、モロッコおよびエジプト南東部のいわゆるパン・アフリカ帯に分布する原生代(約8億年前)のオフィオライト(変動により陸上に露出したある種の海洋底の断片)のマントル部分を研究し、いくつかの重要な知見を得た。構成するかんらん岩は変質/変成が激しく、唯一の残留鉱物であるクロムスピネルより、マントル構成物質がマグマ成分に極めて乏しいことを見いだした。彼は、これらのオフィオライトが前弧域で生成されたと結論した。ワジ・フィコ(エジプト)ではかんらん岩がCO<sub>2</sub>の導入とともに激しく変成されていることを見だし、変成条件の詳しい解析を行なった。また、特異な炭酸塩-斜方輝石岩を原生代オフィオライトで初めて発見した。ボウ・アゼール(モロッコ)では完全に蛇紋岩化(加水化)したかんらん岩中に特異な磁鉄鉱脈を見だし、蛇紋岩化に伴う鉄の移動に関する重要な解釈を加えた。また、蛇紋岩中のクロムスピネルを詳しく解析し、蛇紋岩化に伴うニッケル、コバルト、マンガンの移動性に関して重要な知見をもたらした。ガハラン君の成果は、原生代のオフィオライト成因のみならず、かんらん岩の加水化の際の元素移動や鉱床形成論に対する貢献が極めて大きいと判断される。よって、本審査委員会は全員一致で、本論文がガハラン君に博士(学術)の学位を与えるのにふさわしいものと判断する。