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Spinel composition as a petrogenetic indicator of the mantle section in the Neoproterozoic Bou Azzer ophiolite, Anti-Atlas, Morocco

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Abstract

The Neoproterozic Bou Azzer ophiolite, Anti-Atlas, Morocco, is one of the best preserved ophiolites of Neoproterozic age. However, due to severe serpentinization, almost all primary minerals have been converted to secondary minerals except chromian spinel which has survived alteration in ultramafic rocks and is used here as the only reliable petrogenetic indicator. Relics of the primary textures indicate that the mantle section at Bou Azzer is composed mainly of harzburgite with dunite lenses and veins and small scale chromitite pods. Wehrlite is also found as late-stage intrusions into the mantle section and still has preserved the primary silicates, olivine and clinopyroxene. The chromian spinel chemistry in both peridotite rocks and chromitite pods exhibits a very limited compositional range. The Cr# [= Cr/(Cr + Al) atomic ratio] of spinel is about 0.8 in all serpentinized peridotites and ranges from 0.65 to 0.85 in chromitites, while it is slightly lower, about 0.6, in wehrlite. This suggests the upper mantle from which the Bou Azzer peridotite had been derived was highly refractory. The frequent occurrence of the highly refractory mantle in Precambrian ophiolites may indicate that the high-degree partial melting was much more common in the Precambrian era. © 2005 Elsevier B.V. All rights reserved.

Keywords: Bou Azzer; Morocco; Neoproterozoic; Ophiolite; Mantle section; Chromian spinel

1. Introduction

Ophiolite is an important tool for understanding the tectonic and magmatic processes for oceanic litho-

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sphere formation throughout the time. The lithologicalchemical signatures of the mantle section can provide further insights into the tectonic setting at which the complex was formed; supra-subduction setting or midocean ridge setting. Numerous studies have been done on the various Phanerozoic ophiolites, whereas the data on the Precambrian ophiolites are scarce and fragmentary. This may be due to the extensive dismembering

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and metamorphism of the ophiolitic rocks of older ages which lead to obliteration of their initial characters. More details about the petrological characteristics of the Precambrian ophiolites are needed to estimate the change of thermal regime, if any, of the crust-mantle evolution system from the late Precambrian to Phanerozoic. Thus, a well-preserved and relatively undisturbed ophiolite of Precambrian age will be of particular geologic importance. Very few petrological studies have been achieved on the Precambrian ophiolites, in general (Quick, 1990; Bonavia et al., 1993; Liipo et al., 1995; Vuollo et al., 1995; Suita and Strieder, 1996; Ahmed et al., 2001), and on the late Proterozoic ophiolite at Bou Azzer, Morocco, in particular (Leblanc, 1976, 1981; Bodinier et al., 1984). As the Bou Azzer ophiolite has almost undisturbed ophiolite stratigraphy, the petrological characteristics of its individual members are of prime importance to understand geodynamics of that age.

This article is the first descriptive report on the petrological characteristics of the mantle section of the late Precambrian Bou Azzer ophiolite, Anti-Atlas, Morocco. We try to describe the primary lithology of the mantle section based on the relic textures and to specify its primary petrological properties using intact spinel compositions.

2. Geological background

The Bou Azzer ophiolite constitutes the Proterozoic Anti-Atlas orogenic belt of southern Morocco, with other massifs such as Ifni, Kerdous, Akka, Sirwa, Saghro, and Ougnat (Fig. 1) (Ennih and Liégeois, 2001). The Anti-Atlas Mountains are composed of a Precambrian crystalline basement unconformably overlain by a platform of sedimentary sequence (Leblanc, 1981). The Anti-Atlas orogenic belt forms the boundary between the two major tectonic parts, the Eburnian or West African craton (2000 Ma) basement rocks to the southwest and the Pan-African (700-600 Ma) crystalline basement to the northeast (e.g. Saquaque et al., 1989; Ennih and Liégeois, 2001). The Bou Azzer ophiolite, located about 300 km to the east of Agadir city, is about 60 km long and 5 km wide in plan (Fig. 1). It exhibits an ophiolitic sequence of



Fig. 1. Main geological units of the Anti-Atlas belt, Morocco, showing the location of Bou Azzer ophiolite. The inset shows the location of Bou Azzer area in Morocco, north-west Africa (after Cheilletz et al., 2002).



Fig. 2. Geological sketch map showing the major rock units of the Neoproterozoic ophiolite complex at Bou Azzer area, Morocco (after Bodinier et al., 1984).

5 km in thickness and comprises the following rock units (Figs. 2 and 3) in ascending order; upper mantle tectonite peridotites (about 2 km), mafic-ultramafic cumulates (layered gabbro, about 500 m), submarine basaltic pillow lavas (about 500 m), diorite to quartz diorite, and volcanosedimentary sequence (about 1500 m) (Leblanc, 1976; Bodinier et al., 1984). Almost all rocks were metamorphosed to greenschist facies during the Pan-African orogeny (Bodinier et al., 1984).

The serpentinized mantle peridotite is the dominant rock type in the Bou Azzer ophiolite, forming about 40% of the total complex, and we have discontinuous but good outcrops of peridotite in the Bou Azzer district. The samples for our study were collected at three localities to represent the mantle section of the ophiolite (Fig. 2). Due to severe serpentinization, almost all primary silicate minerals have been extinguished in ultramafic rocks, and the contact between the mantle peridotite and the overlaying ultramafic cumulates is not clearly defined (e.g. Leblanc, 1976). There are some ultramafic dikes and sills of dunite-wehrliteclinopyroxenite compositions that crosscut the mantle peridotite (Leblanc, 1976).

3. Petrography of ultramafic rocks

Depleted harzburgite is the most dominant constituent of the mantle section of the Bou Azzer ophiolite (Leblanc, 1981; Bodinier et al., 1984), recalling the mantle of the late Precambrian ophiolite complexes of Egypt (Ahmed et al., 2001; Ahmed and Arai, submitted for publication). The serpentinized peridotite at Bou Azzer is composed mainly of antigorite serpentine, talc, carbonate, chlorite and subordinate amounts of spinel (<1%). A small amount (ca. 10%) of bastite, possibly a pseudomorph after orthopyroxene, is found in the peridotite, indicating a depleted harzburgite protolith (Fig. 4A). Spinel exhibits anhedral to subhedral, and sometimes complicated in shape (Fig. 4B), and shows fresh core and altered rim. The characteristic feature of the Bou Azzer ophiolite, as in other Late Proterozoic ophiolites, e.g. from Eastern Desert, Egypt (Ahmed et al., 2001; Ahmed and Arai, submitted for publication), is carbonatization of the mantle serpentinized peridotites. Carbonate (=dolomite) occasionally encloses sulpharsenide (gersdorffite; NiAsS) and sulphide (chalcopyrite) grains in harzburgite (Fig. 4C).



Fig. 3. Simplified lithological column showing the stratigraphy of the late Precambrian Bou Azzer ophiolite, Anti-Atlas, Morocco (after Leblanc, 1981).

Dunite is occasionally found as envelopes around small scale chromitite pods and as veins and dikes throughout the harzburgite mass. Antigorite serpentine, talc, chlorite and carbonate are the main minerals in the serpentinized dunite. Some dunite contains irregular-shaped saussurite, possibly indicating melt impregnation. Chromian spinel in dunite attains to about 2% in volume and exhibits euhedral to subhedral shapes (Fig. 4D) with intact core and optically distinct altered rim. The lack of bastite and equant shape of spinel enable us to distinguish dunite with harzburgite. Small chromitite pods range from few centimeters up to 10 m in size. Chromitite shows massive textures with approximately fresh spinel grains almost free of alteration (Fig. 4E). The silicate matrix is composed mainly of chlorite, antigorite, and magnetite. Primary silicate inclusions have been altered to chlorite and/or serpentine.

Wehrlite contains a notable amount of amphibole. Primary olivine and clinopyroxene are slightly altered to serpentine and amphibole. Chromian spinel, less than 1% in volume, shows anhedral to rounded shape and has intact core and altered Cr-rich magnetite rim with a sharp optical boundary (Fig. 4F).

4. Mineral chemistry

Mineral analyses were carried out at the Centre for Co-operative Research of Kanazawa University, Japan, using a JEOL JXA-8800 electron probe microanalyzer. The analytical conditions were a 25 kV accelerating voltage, 20 nA probe current and 3 μ m probe diameter. The raw data were corrected using an on-line ZAF program. The ferric and ferrous irons of spinel were calculated assuming spinel stoichiometry. The Cr# is Cr/(Cr + Al) atomic ratio. The Mg# is Mg/(Mg + total Fe) atomic ratio for silicates, and is Mg/(Mg + Fe²⁺) atomic ratio for spinel. Selected microprobe analyses are listed in Table 1.

Chromian spinel shows a very high and restricted range of Cr content in harzburgite (Table 1). The Cr_2O_3 content of spinel is 59.36 wt.% on average, and the Cr# is 0.80 on average in harzburgite (Table 1 and Fig. 5). TiO₂ content of spinel in harzburgite is very low, <0.1 wt.% (Table 1). The altered rim of spinel is Cr-bearing magnetite (Fig. 5).

Chromian spinel also shows a uniform and confined composition of range for Cr#, ~ 0.85 in dunite (Table 1 and Fig. 5). Altered spinel rim is also Cr-bearing magnetite in dunite (Fig. 5).

Chromian spinel occasionally shows distinct compositional zonations from a Cr-rich core and Fe-rich rim

Fig. 4. Electron micrographs and photomicrographs of harzburgite, dunite, chromitite and wehrlite of the Bou Azzer ophiolite, Anti-Atlas, Morocco. (A) Bastite pseudomorph showing magnetite striations after the pre-existing cleavage of orthopyroxene in mantle harzburgite (sample no. SR21). Plane-polarized light. (B) Anhedral shape of chromian spinel in mantle harzburgite (sample no. SR22). Crossed-polarized light. (C) Electron micrograph of chalcopyrite (Cp) and gersdorffite (Gr) within dolomite of altered mantle harzburgite (sample no. SR22). (D) Euhedral to subhedral chromian spinel grains in carbonatized serpentinized dunite (sample no. VSP). Plane-polarized light. (E) Chromian spinel in massive chromitite (sample no. CR25). Note the fractured but chemically intact nature of spinel. Plane-polarized light. (F) Electron micrograph of a zoned chromian spinel grain showing the intact spinel core and Cr-rich magnetite rim (Cr–Mg) in wehrlite (sample no. BP1).













Table 1

Chromitite Wehrlite Harzburgite Dunite **SR21 SR22** VSP **CR21 CR23 CR25** BP1 SiO₂ 0.00 0.00 0.02 0.00 0.00 0.07 0.00 TiO₂ 0.07 0.02 0.06 0.03 0.05 0.07 0.04 10.99 18.39 Al₂O₃ 9.88 6.73 12.16 8.72 16.15 Cr_2O_3 57.73 60.01 58.07 57.94 51.44 62.06 36.93 16.04 18.29 20.79 12.46 10.76 13.81 FeO 25.732.97 3.38 Fe₂O₃ 1.07 2.36 6.58 2.02 15.59 4.93 0.93 0.88 0.82 0.99 MnO 1.58 1.09 MgO 8.95 9.89 7.88 13.47 15.88 12.18 5.47 0.01 CaO 0.02 0.01 0.00 0.00 0.000.01 Na₂O 0.01 0.00 0.00 0.00 0.02 0.02 0.00 K₂O 0.02 0.03 0.03 0.03 0.02 0.02 0.02 NiO₂ 0.05 0.03 0.03 0.09 0.19 0.07 0.10 Total 99.88 102.10 101.12 100.03 100.96 100.03 101.13 No. of atoms, O = 4Si 0.000 0.000 0.001 0.000 0.000 0.002 0.000 Ti 0.002 0.000 0.001 0.001 0.001 0.002 0.001 Al 0.434 0.385 0.275 0.457 0.664 0.334 0.664 Cr 1.527 1.568 1.591 1.486 1.271 1.621 1.018 Fe²⁺ 0.557 0.520 0.613 0.368 0.282 0.413 0.766 Fe³⁺ 0.047 0.080 0.060 0.175 0.073 0.051 0.418 Mn 0.140 0.044 0.027 0.024 0.021 0.027 0.032 0.725 Mg 0.446 0.487 0.407 0.640 0.590 0.284 Ca 0.001 0.000 0.000 0.000 0.000 0.000 0.000 Na 0.001 0.000 0.000 0.000 0.001 0.001 0.000 Κ 0.001 0.001 0.001 0.001 0.001 0.001 0.001 Ni 0.001 0.001 0.001 0.002 0.004 0.001 0.002 Total 3.623 3.604 3.853 3.470 3.394 3.483 4.342 Cr 0.779 0.803 0.853 0.765 0.657 0.829 0.605 0.445 0.484 0.399 0.635 0.321 0.588 0.271 Mg#

Representative microprobe analyses of chromian spinel in harzburgite, dunite, chromitites, and wehrlite of the Late Proterozoic Bou Azzer ophiolite, Morocco

SR21, SR22, VSP, CR21, CR23 CR25 and BP1 represent the sample numbers. $Cr\# [Cr/(Cr + Al) \text{ atomic ratio}], Mg\# [Mg/(Mg + Fe^{2+}) \text{ atomic ratio}].$

in wehrlite (Fig. 5). The spinel core contains 33.2 wt.% of Cr₂O₃, 16.8 wt.% of Al₂O₃, and 41.3 wt.% of FeO^{*} as total Fe (Table 1). TiO₂ content is also very low, 0.08 wt.% on average, in wehrlite spinel (Table 1). The Mg# of olivine, clinopyroxene and hornblende amphibole is relatively low, 0.86, 0.93, and 0.91, respectively.

Chromian spinel analyzed for three chromitite pods (CR21, CR23, CR25) exhibits very uniform compositions in individual pods (Fig. 6). The Cr# is 0.66, 0.76, and 0.83 on average in the pods CR23, CR21 and CR25, respectively (Table 1 and Fig. 6). The spinel is generally very low in Fe³⁺ ratio, all the analyses being located adjacent to the Cr–Al join reflecting the unaltered character (Fig. 6). The TiO₂ content is very low, <0.06 wt.% on average, in the chromitite spinel (Table 1). The MnO

content of the chromitite spinel is slightly high and is usually around 0.8–0.9 wt.% (Table 1).

Chlorite and antigorite in chromitite are highly magnesian, and the Mg# is 0.99 and 0.98 for chlorite and antigorite, respectively. The averaged Mg# of antigorite is 0.97 in harzburgite and 0.95 in dunite. Dolomite is the main carbonate present both in the chromitite and peridotite, and its Mg# is 0.98 on average.

5. Discussion

5.1. Tectonic implications

As far as we know there have been no petrological studies on the mantle section of the Neopro-



Fig. 5. Cr–Al–Fe³⁺ atomic ratios of chromian spinel in mantle harzburgite, dunite and wehrlite of Bou Azzer ophiolite complex, Anti-Atlas, Morocco. Spinel compositional fields of mantle harzburgite of the Neoproterozoic ophiolites, *solid line field*, of the southern Eastern Desert, Egypt (Ahmed et al., 2001; Ahmed and Arai, submitted for publication), and Wadi Onib of the northern Red Sea hills of the Sudan (Hussein et al., 2004), and Phanerozoic mantle peridotites, *black field*, are used for comparison. Average composition of spinel of mantle harzburgite of the early Proterozoic Outokumpu – Jormua ophiolite, *filled square* symbol (Liipo et al., 1995; Vuollo et al., 1995), Papuan ophiolite, Papua-New Guinea, *filled star* symbol (e.g. England and Davies, 1973; Jaques and Chappell, 1980), and Kamuikotan ophiolite, Hokkaido, Japan, *open star* symbol (Tamura et al., 1999), are also used for comparison.

terozoic Bou Azzer ophiolite. The chromian spinel in most cases survives metamorphism and can be used as the only reliable key mineral of the primary mantle lithology even in altered Precambrian ultramafic rocks (e.g. Liipo et al., 1995). The Cr# of spinel of spinel peridotite is basically controlled by the degree of partial melting (Dick and Bullen, 1984; Arai, 1994a). The degree of partial melting, including second-stage melting (Duncan and Green, 1980), enhances the Cr# of spinel in the peridotite restite (Dick and Bullen, 1984; Arai, 1994a). The melting style of the upper mantle is possibly different from a tectonic setting to another, which gives rise to the difference of degree of melting of peridotite depending on the tectonic setting; arc, plume or mid-ocean ridge (Dick and Bullen, 1984; Arai, 1994a). The highly depleted peridotite with high-Cr# (>0.7) spinel can be produced either at the mantle wedge beneath arcs or at the plumerelated within-plate mantle (e.g. Pearce et al., 1984; Arai, 1994b; Ishiwatari et al., 2003).



Fig. 6. Cr–Al–Fe³⁺ atomic ratios of chromian spinel in chromitite pods in Bou Azzer ophiolite complex, Anti-Atlas, Morocco. Note the very restricted spinel composition for each pod. Spinel compositional field represents chromitites of the Neoproterozoic ophiolites of the central to southern Eastern Desert, Egypt, and the Wadi Onib of the Sudan. The average spinel composition of Kenticha Hill chromitite, Ethiopia, *star* symbol, is also used for comparison.

In addition to the high-Cr# of spinel, the depleted nature of the Bou Azzer ophiolite mantle section can be also deduced from the low modal amount of orthopyroxene pseudomorphs (\sim 10%) in harzburgite. In spite of the high degree of serpentinization, pyroxene pseudomorphs (bastite) are still preserved (see Fig. 4A). The modal amount of pyroxene pseudomorphs is estimated in five thin sections, none of them exceeds 10% of the whole mineral constituents. Due to the high refractory nature of spinel in this rock, pyroxene should be orthopyroxene rather than clinopyroxene. According to the phase relations in the simple peridotite system (e.g. Kushiro, 1969), the amount of residual orthopyroxene decreases rapidly after disappearance of clinopyroxene upon partial melting (e.g. Dick and Fisher, 1984). The TiO₂ content of spinel in the magma varies depending on the tectonic setting of generation: it is the lowest for the arc magma, intermediate for MORB and the highest for the intraplate magma (Arai, 1992). The depleted harzburgite with high-Cr#, low-TiO₂ spinel from Bou Azzer suggests an origin from the mantle wedge or sub-arc mantle. The suite of depleted ultramafics, i.e. harzburgite, dunite and chromitites, from the Bou Azzer ophiolite may have had a genetic linkage with boninitic magma or high-Mg arc tholeiite. The Neoproterozoic ophiolite of Bou Azzer, Morocco is possibly a fragment of arc lithosphere that has formed or has been modified from a precursor (e.g. oceanic lithosphere) at a supra-subduction zone environment.

We, therefore suggest that the production of highly depleted peridotite and related rocks, i.e. the high degree of partial melting, was much more prevalent in the Precambrian time than in the Phanerozoic time. We need accumulation of much more data from Precambrian ophiolites to examine the secular change of degree of melting with the earth's mantle throughout the earth's history.

5.2. Comparison with other Proterozoic and Phanerozoic ophiolites

Compared with Archean and Phanerozoic equivalents, Neoproterozic ophiolite complexes provide unique information about the secular evolution, if any, of the crust-mantle system (Waston, 1978; Stowe, 1994). Most of the well known ophiolite complexes are mainly late Paleozoic to Mesozoic in age; however there have been few studies on the older ophiolites of Archean and Neoproterozic ages (e.g. Leblanc, 1981; Quick, 1990; Bonavia et al., 1993; Liipo et al., 1995; Vuollo et al., 1995; Zimmer et al., 1995; Suita and Strieder, 1996; Ahmed et al., 2001; Kusky et al., 2001; Hussein et al., 2004). For example, there are no petrological data available on the mantle section of the Dongwanzi ophiolite, northern China, of Archean age (2.51 Ga), that has a nearly complete ophiolite section (Kusky et al., 2001). Some petrological data on the mantle section are available from younger ophiolites, i.e., the Outokumpu-Jormua ophiolite of early Proterozoic age (1.96 Ga) (Liipo et al., 1995; Vuollo et al., 1995) and Neoproterozoic ophiolites (Quick, 1990; Bonavia et al., 1993; Ahmed et al., 2001; Hussein et al., 2004).

The highly depleted mantle harzburgite with high-Cr# (>0.7) of chromian spinel; however is very rare in Phanerozoic ophiolites. Most of mantle harzburgites have a wide spinel composition, Cr# varies from 0.2 up to 0.7 (Fig. 5) with an average of intermediate Cr# of spinel, around 0.5, and are the most common host for large podiform chromitites in Phanerozoic ophiolites (e.g., Arai, 1997 and references therein). The mantle peridotite of Neoproterozoic Bou Azzer ophiolite is more refractory than the vast majority of those in the Phanerozoic ophiolites. Two exceptions are the Papuan ophiolite, Papua-New Guinea (e.g. England and Davies, 1973; Jaques and Chappell, 1980), which have a depleted harzburgite with high-Cr# of spinel, ≥ 0.9 (Fig. 5), and the Kamuikotan ophiolites, Hokkaido, Japan (e.g. Tamura et al., 1999) which have a highly refractory mantle harzburgite with Cr# of spinel ranging from 0.64 to 0.92, of 0.75 on average (Fig. 5).

The high refractory nature of the Neoproterozoic Bou Azzer ophiolitic peridotite, on the other hand, is shared by several Precambrian ophiolites. The high-Cr# of spinel (Cr# > 0.8, Fig. 5) of the mantle tectonites of the early Proterozoic Outokumpu - Jormua ophiolite (Liipo et al., 1995; Vuollo et al., 1995) may indicate a high degree of melting of peridotite or, alternatively, re-melting of a previously depleted peridotite. Spinel compositions of the mantle harzburgite, dunite and chromitites of the Neoproterozoic ophiolite in the southern to central Eastern Desert, of Egypt, and the Wadi Onib Neoproterozoic ophiolite, northern Red Sea hills of the Sudan (Cr# ranging from 0.5 to 0.85, Figs. 5 and 6), also show a highly depleted nature of the mantle (e.g., Ahmed et al., 2001; Ahmed and Arai, submitted for publication; Hussein et al., 2004). Spinel from the Neoproterozoic podiform chromitite deposits from the Kenticha Hill, Ethiopia (Bonavia et al., 1993) also has high-Cr#s (≥ 0.9) (Fig. 6).

The petrological characteristics of the mantle section of the Bou Azzer ophiolite, i.e. highly depleted nature of peridotite and high-Cr# of spinel in chromitite, are quite common to other ophiolites of Neoproterozoic age (Figs. 5 and 6), e.g. ophiolites from the Eastern Desert of Egypt (Ahmed et al., 2001; Ahmed and Arai, submitted for publication), Wadi Onib, northern Red Sea hills of the Sudan (Hussein et al., 2004), Kenticha Hill, Ethiopia (Bonavia et al., 1993), and Saudi Arabia (e.g. Quick, 1990).

6. Conclusions

The mantle section of Bou Azzer ophiolite of Proterozoic age is mainly composed of highly depleted harzburgite with low orthopyroxene content (\sim 10%) and high-Cr# (\sim 0.8) spinel. Associated dunite and chromitite also contain high-Cr# (0.7–0.8) spinel. Combined with the extremely low TiO₂ (<0.1 wt.%) character of spinel, we conclude that the formation of Bou Azzer ophiolite may have been linked with some high-Mg, high-Cr supra-subduction zone magma, such as high-Mg andesite, boninite or high-Mg tholeiite. The depleted harzburgite is common to the Neoproterozoic ophiolites, suggesting high degree of partial melting was prevalent in the Neoproterozoic era.

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