The chromitites of the Neoproterozoic Bou Azzer ophiolite (central Anti-Atlas, Morocco) revisited

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ABSTRACT

The Neoproterozoic Bou Azzer ophiolite in the Moroccan Anti-Atlas Panafrican belt hosts numerous chromitite orebodies within the peridotite section of the oceanic mantle. The chromitites are strongly affected by serpentinization and metamorphism, although they still preserve igneous relicts amenable for petrogenetic interpretation. The major, minor and trace element composition of unaltered chromite cores reveal two compositional groups: intermediate-Cr (Cr# = 0.60 – 0.74) and high-Cr (Cr# = 0.79 – 0.84) and estimates of parental melt compositions suggest crystallization from pulses of fore-arc basalts (FAB) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle. A platinum group elements (PGE) mineralization dominated by Ir-Ru-Os is recognized in the chromitites, which has its mineralogical expression in abundant inclusions of Os-Ir alloys and coexisting magmatic laurite (RuS2) and boninitic melts, respectively, that infiltrated the oceanic supra-subduction zone (SSZ) mantle.
1. Introduction

The presence of chromitites is one of the characteristics shared by most ophiolites worldwide (Leblanc and Nicolas, 1992 and references therein). These bodies of rocks made almost exclusively by chromite are usually hosted in peridotites that represent the upper mantle section of the ophiolite (e.g., González-Jiménez et al., 2014a; Arai and Miura, 2016). Recent observation of unusual (“exotic”) mineral assemblages (Table 1) typical of continental crust rocks (e.g., Yamamoto et al., 2013; Robinson et al., 2015; Gahlan et al., 2006; El Hadi et al., 2010; Ahmed et al., 2005; Gahlan et al., 2006; El Hadi et al., 2010). Furthermore, the identification of continental-derived zircons in some ophiolitic chromitite orebodies (e.g., Arai and Miura, 2018). The Bou Azzer ophiolitic sequence, located in the Panafrican Anti-Atlas belt of Morocco (Fig. 1a), a sequence of layered gabbros (~500 m) and pillow lavas (~500 m) intruded by a quartz-diorite stock overlain by a thick, Ediacaran to Cambrian volcano-sedimentary sequence (~1500 m) including the syn-orogenic Tididline clastic Formation (Leblanc, 1972, 1975, 1981; Bodinier et al., 1984; Hefferan et al., 2002; Soulaimani et al., 2002; Triantafyllou et al., 2018, 2020; Hodel et al., 2020) vs. back-arc position (e.g., Bodinier et al., 1984; Arai and Miura, 2018). The presence of chromitite orebodies in this region has been extensively studied since the 1970s (e.g., Leblanc, 1972, 1975, 1981; Leblanc and Nicolas, 1992 and references therein). There is still great uncertainty and limited information regarding the less-abundant Archaean and Proterozoic ophiolitic chromitites. The Bou Azzer ophiolitic sequence is intruded by two groups of arc-related (e.g., Arai and Ahmed, 2018). The general assumption is that these chromitites and their hosting mantle peridotites formed in a supra-subduction zone (SSZ) setting (Bodinier et al., 1984; Naidoo et al., 1991; Ikenna et al., 2005; Ahmed et al., 2005; El Hadi et al., 2010; Walsh et al., 2012; Arenas et al., 2020) vs. back-arc position (e.g., Bodinier et al., 1984; Triantafyllou et al., 2018; Hodel et al., 2020) is still debated. Recently, Arenas et al. (2020) identified MORB-like and boninitic compositions within the mafic rocks of the Bou Azzer crustal sequence, and interpreted that the ophiolite formed in a subduction-initiation geodynamic setting, where magmas evolve from MORB-like (FAB) to boninitic-like as subduction proceeds (Whattam and Stern, 2011). This paper aims to propose a genetic model for the Bou Azzer chromitites in the context of the complex evolution of their host ophiolite with new petrographic, mineralogical and geochemical data combined with previous knowledge. We provide the first-ever trace element data for chromite forming these chromitites as well as a detailed characterization of mineral phases within chromitite not previously reported, including PGM, minerals of the SuR-nominally UHP association such as moissanite (SiC), native Cu and silicates (oriented clino- pyroxene lamellae), and exotic minerals such as zircon and diaspore. Furthermore, we compare the Bou Azzer chromitites with other published data of Precambrian ophiolitic chromitites worldwide.

2. Geological setting

2.1. The Bou Azzer ophiolite

The Bou Azzer ophiolite is located in the central part of the Panafri-

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nican Anti-Atlas belt of Morocco (Fig. 1a). The ophiolitic rocks crop out in the core of a NW-SE directed recumbent antiform (Fig. 1a), affected by folds and thrusts and faults (El Hadi et al., 2010). Even though the ophiolite sequence is highly dismembered, the original description of the ophiolite (Leblanc, 1972, 1975, 1981) exhibits a 4–5 km sequence and comprises from bottom to top: pervasively serpen-
tized upper mantle peridotites (~2000 m) cross-cut by mafic dikes (Fig. 1b), a sequence of layered gabbros (~500 m) and pillow lavas (~500 m) intruded by a quartz-diorite stock overlain by a thick, Ediacaran to Cambrian volcano-sedimentary sequence (~1500 m) including the syn-orogenic Tididline clastic Formation (Leblanc, 1972, 1975, 1981; Bodinier et al., 1984; Hefferan et al., 1992; Thomas et al., 2004; Gasquet et al., 2005; Ahmed et al., 2005; Gahlan et al., 2006; El Hadi et al., 2010).

The age of the ophiolite is still controversial; SHRIMP U-Pb zircon dating yielded 697 ± 6 Ma in a metagabbro located in the Bougmane complex (El Hadi et al., 2010) and LA-ICP-MS U-Pb zircon dating yielded 759 ± 2 Ma in a layered metagabbro from the crustal section at Ait Ahmame (Hodel et al., 2020). These differences suggest that the younger age obtained by El Hadi et al. (2010) may correspond to the volcanic arc stage (Triantafyllou et al., 2018, 2020; Hodel et al., 2020) or may be indicative of a long-lived construction of the oceanic lithosphere. The ophiolitic sequence is intruded by two groups of arc-related granitoids: 1) syn-orogenic granitoids emplaced during arc-continent collision (632–659 Ma; El Hadi et al., 2010; Inglis et al., 2005); 2) Late-orogenic granitoids represented by the Bleida granodiorite dated at 579 Ma (Inglis et al., 2004). Low- to medium-grade metamorphic assemblages overprint the Bou Azzer ophiolite (Leblanc, 1981; Saquaque et al., 1989; Hefferan et al., 2000; El Hadi et al., 2010).

The ophiolitic bodies in the region are interpreted as the suture of the Panafri-

The Neoproterozoic (759 and 679 Ma; El Hadi et al., 2010; Hodel et al., 2020) Bou Azzer ophiolite sequence, located in the Panafri-

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Table 1
Occurrence of ultra-high pressure (UHP), super-reduced (SuR) and crustal-derived unusual phases in ophiolites and chromitites worldwide. Luobusa (Tibet), Dingqing (Tibet) and Ray-Iz (Polar Urals) data are from Yang et al. (2015), Griffin et al. (2016), Xiong et al. (2017a) and references therein, Purang (Tibet) from Yang et al. (2011) and (Xiong et al., 2019), Zedang (Tibet) from Xiong et al. (2017b), Hegenshan (Inner Mongolia) from Huang et al. (2016), Nidar (Ladakh, Himalaya) from Das et al. (2017), Myitkyina (Myanmar) from Chen et al. (2018), Alapaevsk (Russia) from Zaccarini et al. (2016), Semail (Oman) from Miura et al. (2012) and Robinson et al. (2015), Mirdita (Albania) from Xiong et al. (2017c), Pozanti-Karsanti (Turkey) from Lian et al. (2017), Orhaneli-Harmancik (Turkey) from Akbulut (2018), Othyrrys (Greece) from Zaccarini et al. (2019) and Bindi et al. (2020), Baja California (Mexico) from González-Jiménez et al. (2017a), Tehuitzingo (Mexico) from Farré-de-Pablo et al. (2019a), Moa-Baracoa (Cuba) from Proenza et al. (2018), Pujol-Sola et al. (2018), Pujol-Sola et al., 2020a), and Bou Azzer data from the present study. Host rock abbreviations: Chrom – chromitite, Harz – harzburgite, Dun – dunite, Lherz - lherzolite. X - indicates the presence of the mineral in the opholite.

| Ophiolite | Luobusa (Tibet) | Dingqing (Tibet) | Purang (Tibet) | Zedang (Tibet) | Hegenshan (Inner Mongolia) | Nidar (Ladakh, Himalaya) | Myitkyina (Myanmar) | Ray-Iz (Polar Urals) | Semail (Oman) | Mirdita (Albania) | Pozanti-Karsanti (Turkey) | Orhaneli-Harmancik (Turkey) | Othyrrys (Greece) | Baja California (Mexico) | Tehuitzingo (Mexico) | Moa-Baracoa (Cuba) | Bou Azzer (Morocco) |
|-----------|----------------|----------------|----------------|----------------|-----------------------------|--------------------------|---------------------|-------------------|---------------|----------------|-----------------------|--------------------------|---------------------|--------------------------|-----------------|-------------------------|-------------------|
| Host rock | Chrom, Harz    | Harz           | Lherz          | Chrom, Dun     | Harz, Lherz             | Chrom, Harz, Dun, Lherz  | Ray-Iz (Polar Urals)| Alapaevsk (central Urals, Russia) | Chrom | Chrom | Chrom | Chrom | Chrom | Chrom | Chrom | Chrom | Chrom, Harz | Chrom | Chrom | Chrom | Chrom |
| Diamond  | X              | X              |                | X              | X                          | X                        | X                   | X                 | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Coesite/ Stishovite pseudomorph  |                |                |                | X              |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| TiO2-II (α-PbO2 structure)      |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Cubic-BN                           |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Si-rutile                           |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| BWJ (inverse-spinel structure)     |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| CF-chromite Clinopyroxene exsolution lamellae |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Amorphous carbon                   |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Moissanite (SiC)                   |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Fe-carbide (FeC)                   |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| W-carbide (WC)                    |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Ti-carbide (TiC)                    |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Fe-silicide (FeSi)                   |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Ti-nitride (TiN)                    |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| TAZ (Ti4Al2Zr, SiO11)            |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Native Si                          |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Native Ni, Co, Cr, Cu               |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Iron-Wustite (Fe-FeO)               |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Alloys (Fe-Mn, Fe-Cr, Fe-Co)        |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Phosphides                          |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Almandine                          |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Andalusite                          |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Biotite                            |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Corundum                            |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| K-feldspar                          |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Kyanite                            |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Muscovite                           |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Quartz                             |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Rutile                             |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Titanite                            |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
| Zircon                             |                |                |                |                |                            |                          |                     |                   | X             | X              | X                     | X                       | X                   | X                       | X               | X                      | X                 |
Fe oxene (Cr-diopside), calcic amphibole (chromian edenite), and Cr- and Fe-rich spinelites show rare inclusions of olivine, usually serpentinized, clinopyroxenes in massive (Fig. 2 f) to semi-massive (Fig. 2 e) textures and serpentine-rich layers embedded in an altered silicate matrix (Fig. 3 d) and banded chromitites in massive-textured ore, and semi-massive and banded ore to a lesser extent (Figs. 2 and 3) and are usually enveloped by completely serpentinized dunite of variable thickness (El Ghorfi et al., 2007). Massive peridotized harzburgitic mantle peridotites (Fig. 1 a; Ikenne et al., 2005; 2.2. Chromite deposits - Thomas et al., 2002; Walsh et al., 2002, 2012).

The Bou Azzer chromitite orebodies are hosted in pervasively serpentinized harzburgitic mantle peridotites (Fig. 1 a; Ikenne et al., 2005; El Ghorfi et al., 2007; Ahmed et al., 2009). The bodies display elongated irregular shapes from almost tabular to lenticular, with sizes ranging from several cm to few tens of meters, with average length of 3 – 4 m and they are concordant to sub-concordant to the mantellic foliation of the host peridotite (Ahmed et al., 2009). Chromitites predominantly consist of massive-textured ore, and semi-massive and banded ore to a lesser extent (Figs. 2 and 3) and are usually enveloped by completely serpentinized dunite of variable thickness (El Ghorfi et al., 2007). Massive chromitites (Figs. 2a-c and 3a-b) are almost totally formed by chromite (>90 vol%) with minor interstitial altered silicate matrix, semi-massive chromitites ores (Figs. 2e and 3c-d) contain 70–80 vol% chromite crystals embedded in an altered silicate matrix (Fig. 3d) and banded chromitites (Fig. 2d-f) are characterized by alternating chromite-rich layers with massive (Fig. 2f) to semi-massive (Fig. 2e) textures and serpentinite-rich layers. The silicate matrix is formed by secondary minerals, mainly chlorite and serpentine, but also talc, magnetite and carbonates in veins (Ahmed et al., 2009). Chromite crystals in the different textured chromitites show rare inclusions of olivine, usually serpentinized, clinoxyroxene (Cr-diopside), calcic amphibole (chromian edenite), and Cr- and Fe3+-garnet (uwavolite-andradite) (El Ghorfi et al., 2007). The chromite orebodies are crosscut by centimetric veins of massive magnetite (Gahlan et al., 2006; Ahmed et al., 2009), suggesting leaching by a Cl-rich hydrothermal event at temperatures below 350 °C during formation of these late veins (Hodel et al., 2017).

3. Studied samples and analytical techniques

We studied representative samples from three chromitite mining sites in the Bou Azzer ophiolite: Inguijem, Filon 60 and Ait Ahmane (Figs. 1 and 2), including massive chromitites from individual pods (n = 4), semi-massive chromitites (n = 2), banded chromitites (n = 1) and the host dunites. Polished thin sections were studied by optical and electron microscopy using a Quanta 200 FEI XTE 325/D8395 scanning electron microscope (SEM) equipped with an INCA Energy 250 EDS microanalysis system and a JEOL JSM-7100 field-emission SEM at the Centres Científics i Tecnològics de la Universitat de Barcelona (CGITUB). Operating conditions were 20 kV accelerating voltage. Micro-Raman spectra were obtained with a HORIBA JobinYvon LabRam HR 800 dispersive spectrometer equipped with an Olympus BXFM optical microscope at the CGITUB. Non polarized Raman spectra were obtained in confocal geometry by applying a 532 nm laser, using a 100x objective (beam size around 2 µm), with 3–5 measurement repetitions for 10–15 s each. The Si band at ~520 cm⁻¹ was used for calibration. The obtained spectra were processed using the LabSpec® software (JobinYvon; Villeneuve-d’Ascq, France).

Quantitative electron microprobe analyses (EMPA) on chromite and platinum group minerals (PGM) were also conducted at the CGITUB using a JEOL JXA-8230 operating in wavelength-dispersive spectroscopy (WDS) mode. Analytical conditions are described in detail in Appendix 1. X-ray (XR) images of chromite (512 x 512 pixels, 0.52 x 0.52 µm pixel size and 266.24 x 266.24 µm total area) and platinum group minerals (three images of 300 x 300 pixels: 0.22 µm pixel size and 66 x 66 µm total area, 0.08 µm pixel size and 24 x 24 µm total area and 0.1 µm pixel size and 30 x 30 µm total area) were obtained with the same a JEOL JXA-8230 electron microprobe operated at 20 kV and 20 nA in spot mode with focused electron beam and counting time of 20 to 60 ms/pixel. The images were treated with DWinImage software (Torres-Roldan & Garcia Casco, unpublished; see Garcia-Casco, 2007). Minor and trace elements in chromite were analyzed using a Resolution M-50 Excimer laser coupled to a ThermalCap Q c inductively coupled mass spectrometer at the Laboratorio de Estudios Isotópicos (LEI) from the Centro de Geociencias, UNAM (Mexico). The analytical conditions and procedure are described in Appendix 1.

A representative sample (m = 4.2 kg) of massive chromitite from the Inguijem deposit was crushed, sieved and processed using hydroseparation (HS Lab, Universitat de Barcelona; http://www.hs-lab-barcelona.com/) to obtain mineral concentrates. The resulting concentrates were mounted as polished monolayers on resin blocks (SimpliMet 1000) in order to identify mineral phases. Whole-rock platinum-group elements (PGE) analyses were performed on 8 chromitite and 5 dunite
samples at Genalysis Ltd (Perth, Western Australia) after nickel sulfide fire assay collection, following the method described by Chan and Finch (2001). The analytical procedure is described in detail in Appendix 1.

4. Results

4.1. Petrography and mineralogy of chromitites

The chromitites from Bou Azzer consist of chromite in an altered silicate matrix, variations in the relative proportions between chromite and the matrix result in the different observed textures (Fig. 3). The Inguijem orebody only contains massive chromitites, whereas Filon 60 is formed by massive chromitites and semi-massive chromitites. Banded chromitites were only observed in Ait Ahmane, where the chromite-rich layers show either massive or semi-massive textures; hence, these samples have been grouped and are described with the two main types.

Massive chromitites (Fig. 3a-b) are formed by coarse-grained (>500 μm) anhedral chromite that shows reddish to black color, pervasive pull-apart fractures (Fig. 3b) and occasional brecciated textures. The chromite grains are generally unaltered (Fig. 4a-d), with limited alteration in the porous rims (brighter phase under the scanning microscope; Fig. 4b) and along fractures that are occasionally filled by late hematite (Fig. 4b). Chromite grains from the Inguijem chromitite orebody (Fig. 4a-b) and from Ait Ahmane are more altered than in Filon 60 (Fig. 4c-d), where alteration is restricted to very narrow rims (Fig. 4c) and along fractures (Fig. 4d) although some samples show strong brecciation (Fig. 4e).

Semi-massive chromitites (Fig. 3c-d) are formed by subhedral to anhedral chromite crystals (~500 μm) that are slightly to strongly fractured. Darker unaltered cores under the scanning microscope are generally surrounded by altered brighter rims (Fig. 4e-f) and the alteration is also evident evident along fractures. Just as observed in massive chromitites, the alteration is less strong in the semi-massive chromitites from Filon 60 (Fig. 4g-h), where it is very restricted along fractures (Fig. 4g) and occasionally in the rims (Fig. 4h), compared to Ait Ahmane (Fig. 4e-f). Nevertheless, the degree of alteration is higher in semi-massive chromitites (Fig. 4e-h) than in massive varieties (Fig. 4a-d).

A large variety of globular, elongated to lamellae-like inclusions and negative crystals, with sizes ranging from few micrometers to 60 μm with average sizes around 10 μm, have been observed in chromite crystals both from massive and semi-massive chromitites. These contain mainly serpentinized olivine, sulfides (in situ pyrite and sphalerite; galena and arsenopyrite in mineral concentrates) and platinum group minerals (PGM) in chromite; and andradite, millerite and a Pb-Ni-S phase in the altered silicate matrix. Appendix 2 contains the list of accessory minerals identified both in situ and in mineral concentrates.

Fig. 2. Outcrops showing the studied chromitite orebodies. (a) Massive chromitite body in Inguijem. (b) Close up of the massive chromitite in Inguijem. (c) Massive chromitite body from Filon 60. (d) Banded chromitites in Ait Ahmane. (e) Close up of disseminated chromitite in the rims of the massive-banded chromitite bodies of (d). (f) Close up of banded chromitite shown in (d).
4.1.1. Platinum-group minerals

Up to 11 different PGM grains have been distinguished in situ in thin sections or recovered in the mineral concentrates. The grain sizes range from a few to several tens of micrometers (Fig. 5). Laurite (RuS₂) (Fig. 5a-b) and Os-Ir alloys (Fig. 5c-e) are the most abundant phases, followed by a highly heterogeneous Ir-As-S phase, probably irarsite (Fig. 5f). PGM grains show euhedral (Fig. 5a), subhedral (Fig. 5c-f) to anhedral shapes (Fig. 5b) and some grains show partial replacement by secondary PGM (Fig. 5b, e), which can either occur at the rims (Fig. 5e) or within the crystal forming nano-blebs of PGE alloys (Fig. 5b). Furthermore, PGM also occur intergrown with alteration minerals such as chlorite (Fig. 5f).

4.1.2. Unusual mineral assemblages

Less common mineral phases found as inclusions within chromite grains consist of submicrometric clinopyroxene lamellae (up to 22 µm long and <1 µm wide) variably distributed following the (111) crystallographic planes of the unaltered chromite cores (Fig. 6a-c). Raman analyses (Fig. 6c) show spectra compatible with diopside after subtracting the chromite signal, with peaks at 328, 394, 563, 669, 1012 and 1045 cm⁻¹. Diaspore was found associated with hematite and clinochlore inclusions within chromite (Fig. 6d-e). Diaspore and hematite have been identified by Raman spectroscopy and shows the typical peaks at 150, 768, 789, and 965 cm⁻¹ (Fig. 6j). Anhedral grains of native Cu, occasionally including chromite, were also recovered (Fig. 6k). Euhedral to subhedral grains of zircon (n = 6) with sizes between 20 and 50 µm, too small for in situ dating, haveapatite (Fig. 6l) and serpentine inclusions (Fig. 6m). Other inclusions typically found in zircon grains recovered from chromitites, such as quartz, K-feldspar and mica (e.g., Robinson et al., 2015; Proenza et al., 2018), have not been identified in the studied grains. Diaspore was found both in situ and in the mineral concentrates (Fig. 6n).

4.2. Chromite composition

Unaltered chromite cores from the Bou Azzer chromitites have Cr₂O₃ contents ranging from 46.6 to 63.9 wt%, Al₂O₃ from 7.8 to 21.5 wt% and MgO from 9.4 to 18.1 wt% (Fig. 7a; Appendix 3). The Cr# [Cr/(Cr + Al) atomic ratio] is strongly variable, from 0.60 to 0.83, and the Mg# [Mg/(Mg + Fe²⁺) atomic ratio] ranges from 0.60 to 0.84 (Fig. 7b). According to the chemistry, unaltered chromite can be divided in two groups: intermediate-Cr chromite (Cr# = 0.60–0.74 and Mg# = 0.61–0.82; sampled from Inguijem and Ait Ahmane deposits) and high-Cr chromite (Cr# = 0.79–0.84 and Mg# = 0.48–0.66; sampled from Filon 60 deposit; Figs. 1 and 2). The grouping of unaltered chromite into intermediate-Cr (Cr# < 0.75) and high-Cr (Cr# > 0.75) chromite (Fig. 7) better fits with the classification proposed by Liu et al. (2019) for chromitites into three categories: high-Cr, intermediate and high-Al (e.g., Uysal et al., 2016, 2018; Chen et al., 2018; Liu et al., 2019) than with the custom classification into high-Cr (Cr# > 0.6) and high-Al (Cr# < 0.6) (e.g., Arai, 1994; Arai and Miura, 2016).

Altered chromite rims (Fig. 8; Appendices 3 and 4) show higher Cr and Fe²⁺ but lower Al and Mg, than unaltered chromite cores, generally progressing towards Cr-rich chromite. Altered chromite, derived from both intermediate-Cr and high-Cr chromite, reach Cr₂O₃ contents of 70
wt%. The $\text{Fe}^{3+}/[\text{Fe}^{2+}+\text{Fe}^{3+}]$ atomic ratio in the altered porous chromite rims (Appendix 3) remains similar to that of unaltered chromite (Fig. 8), except in semi-massive chromitite samples in which ferrian chromite $\text{Fe}^{2+}(\text{Fe}^{3+},\text{Cr})_2\text{O}_4$ developed. Two clear alteration trends can be observed (Fig. 8): first an increase in Cr followed by an increase in $\text{Fe}^{3+}$. The analyzed hematite is relatively enriched in $\text{Cr}_2\text{O}_3$ (up to 7 wt %; Appendix 3) and represents the final product of alteration.

Minor and trace element compositions of unaltered chromite cores (Fig. 9; Appendix 5) shows low Sc (1–5 ppm) and Ga (18–42 ppm) contents, moderate concentrations of Ti (209–370 ppm) and Co (192–347 ppm), and higher Zn (407–1028 ppm), Ni (565–1425 ppm), V (662–1161 ppm), and Mn (1020–5128 ppm) contents. The Ti and Co contents (Fig. 9) are within the same range for both intermediate-Cr and high-Cr chromite; however, it is remarkable that high-Cr chromite shows lower contents of Ga, V and Ni and higher contents of Mn and Sc compared to intermediate-Cr chromite. Similar relationships were already observed in ophiolitic chromitites showing different compositions in terms of Cr# from Cuba and Dominican Republic by Proenza et al. (2011). The altered chromite rims (Appendix 5) exhibit enrichment (at ppm levels) of Ni, V, Zn, and Mn, which is typically observed in chromitites elsewhere (e.g., Colás et al., 2019 and references therein).

4.3. Platinum group elements (PGE) in the Bou Azzer chromitites

4.3.1. Bulk-rock contents of PGE

Bulk-rock PGE contents in chromitites are between 116 and 313 ppb (Appendix 6), being the IPGE (Ir-Os-Ru: 94–265 ppb) more abundant than PPG (Pd-Pt-Rh: 11–48 ppb). Chondrite-normalized patterns
show a positive slope to flat line from Os to Ru and a negative slope from Ru to Pd. In addition, four samples show a negative anomaly in Pt (Fig. 10a). These results compare well with previous data from the Bou Azzer chromitites (El Ghorfi et al., 2007; Ahmed et al., 2009). PGE contents in the host dunites are low ($\Sigma$PGE = 3–30 ppb; Appendix 6), especially compared with previous results by Ahmed et al. (2009), who reported PGE values in the Bou Azzer host-rocks of chromitites ranging from 22 to 60 ppb. In general, the Bou Azzer dunites hosting the chromitites show a positive slope from Os to Ru and a negative slope from Ru to Pd (Fig. 10b), but they do not show preferential enrichment in IPGE nor PPGE.

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4.3.2. Platinum group minerals (PGM) composition

Four grains of alloys from the Bou Azzer chromitites were analyzed by electron microprobe (Appendix 7) and classify mostly as native Os with relevant concentration of Ir (Fig. 11a). The average composition is between Os$_{0.70}$Ir$_{0.23}$Ru$_{0.05}$Pt$_{0.02}$ and Os$_{0.44}$Ir$_{0.39}$Ru$_{0.17}$ (Appendix 7). The chemical composition of magmatic laurite is very close to the laurite end-member composition (Ru$_2$S$_2$; Fig. 11b), containing low amounts of Os and Ir in solid solution, up to 6.70 and 3.18 wt%, respectively (Appendix 7). Laurite shows low PPGE contents, up to 1.16 wt% Rh, 0.43 wt% Pd and 0.51 wt% Pt. The composition ranges from (Ru$_{0.98}$Ir$_{0.02}$Os$_{0.02}$Rh$_{0.02}$)$_{1.00}$ to (Ru$_{0.96}$Os$_{0.08}$Ir$_{0.02}$Rh$_{0.02}$)$_{1.00}$ (n = 15; Appendix 7). X-ray maps of a single magmatic idiomorphic laurite grain (Appendix 8a) show...
Fig. 6. Unusual mineral phases identified in the Bou Azzer chromitites. (a) Oriented clinopyroxene lamellae hosted within chromite (backscattered electron image). (b) Close up of a clinopyroxene lamellae (backscattered electron image). (c) Raman spectra of (from top to bottom) clinopyroxene inclusion within chromite, chromite host and the processed spectra that corresponds to diopside. (d) Mineral inclusions within a chromite grain (backscattered electron image). (e) Close up of one inclusion in (d) that hosts clinohlore, diaspore and hematite (backscattered electron image). (f) Raman spectra of the different minerals in the inclusion in (e) showing the typical spectra of diaspore and hematite. (g) Inclusion trails in chromitite (backscattered electron image). (h) Close up of (g) showing in detail one of the inclusion trails filled by clinohlore (backscattered electron image). (i) Moissanite grain within a mineral concentrate obtained by hydroseparation (backscattered electron image). (j) Raman spectrum of the moissanite grain. (k) Native Cu attached to chromite (backscattered electron image). (l) Subhedral zircon grain with an apatite inclusion (backscattered electron image). (m) Anhedral zircon grain with a serpentine inclusion (backscattered electron image). (n) Euhedral diaspore grain in a mineral concentrate (backscattered electron image). Abbreviations: Chr – chromite, Cpx – clinopyroxene, Clc – clinohlore, Dsp – diaspore, Hem – hematite, Moi – moissanite, Cu – native Cu, Ap – apatite, Zrn – zircon, and Srp – serpentine.
Fig. 7. Composition of the Bou Azzer unaltered chromite cores. (a) \( \text{Al}_2\text{O}_3 \) (wt. %) vs. \( \text{Cr}_2\text{O}_3 \) (wt. %). (b) \( \text{Cr}^\# \) [\( \text{Cr}/(\text{Cr} + \text{Al}) \)] vs. \( \text{Mg}^\# \) [\( \text{Mg}/(\text{Mg} + \text{Fe}^2+) \)]. Dashed lines represent the composition of olivine in equilibrium with chromite at 1200 °C (Dick and Bullen, 1984). (c) \( \text{Cr}^\# \) vs. \( \text{TiO}_2 \) (wt. %). Data sources for chromian spinel of different tectonic settings are Irvine (1967), Leblanc and Nicolas (1992), Arai (1992), Bonavia et al. (1993), Kamenetsky et al. (2001), and Pujol-Sola et al. (2007).

significant zoning. Electron microprobe analyses revealed that some laurite grains are partially altered, showing Ru concentrations up to 70.21 wt%, Os between 1.61 and 4.93 wt%, Ir between 1.06 and 2.82 wt %, up to 1.42 wt% Rh, up to 0.50 wt% Pt, and up to 0.34 wt% Pd (Appendix 7). One grain of altered laurite shows an inverse correlation between Ru and S contents, indicating the transformation of the sulfide into an alloy (X-ray maps of Appendix 8b). A third type of PGM is observed surrounding the alloys (Figs. 5e-f, Appendix 8c), sometimes intergrown with silicates. This phase was too heterogeneous to obtain a well-defined composition, but the analyses confirm the presence of Ir-As-S, probably corresponding to secondary irarsite.

5. Discussion

In this section, petrological, mineralogical and geochemical data are discussed in order to explore the effects of alteration on element mobility, to determine the parental melts for chromitites, to examine the origin and significance of PGE/PGM and unusual mineral phases within the chromitites, to compare with other Precambrian chromitites, and to ultimately provide a genetic model for the formation of the Bou Azzer chromitites.

5.1. Effects of metamorphism and alteration on mobility of major and minor elements

As the Bou Azzer ophiolite is variably affected by post-magmatic processes, including metamorphism, serpentinization and carbonation (e.g., Gahlan et al., 2006; Fanlo et al., 2015; Hodel et al., 2017), interpretations based on the composition of chromite in terms of primary magmatic processes require an assessment of the potential effects of alteration on element mobility. The intermediate-Cr chromite core phases are partially mantled by wide rims of porous altered chromite (Fig. 4b, e-f; Appendix 4), which is texturally very similar to the “porous chromite” reported in chromitites affected by greenschist to amphibolite-facies metamorphism elsewhere (e.g., Gervilla et al., 2012; González-Jiménez et al., 2015a, 2015b, 2017b; Colás et al., 2016, 2019; Hernández-González et al., 2020). The “porous chromite” in the Bou Azzer chromitites is enriched in Cr and Fe\(^{2+}\) and depleted in Al and Mg when compared to the unaltered chromite cores (Fig. 8; Appendix 3). On the other hand, alteration is restricted to thin homogeneous ferrian chromite rims in high-Cr chromitite (Fig. 4c, h). Semi-massive chromitites show more evolved alteration than massive chromitites due to stronger interaction (i.e. lower chromite/silicate ratio) with the fluids altering the host peridotites (e.g., Proenza et al., 2004; González-Jiménez et al., 2015a; Gervilla et al., 2012; Colás et al., 2019).

The textural and chemical evidences suggest two different stages of alteration (Fig. 8), similar to the alteration reported in many other ophiolitic chromitites (Proenza et al., 2004; Gervilla et al., 2012; Colás et al., 2014, 2019, 2020; González-Jiménez et al., 2015a, 2015b, 2017b; Hernández-González et al., 2020): first, Cr and Fe\(^{2+}\) increase under water-saturated reduced conditions accompanied by a volume reduction of ~43% (Gervilla et al., 2012) in order to form the porous chromite (Fig. 8a); and afterwards, oxidizing conditions prompt the formation of ferrian chromite (Fig. 8b). A latter stage of alteration involved the circulation of Fe\(^{3+}\)-rich fluids that formed Cr-magnetite, as reported in the Bou Azzer serpentinites by Hodel et al. (2017). This magnetite veins were later oxidized forming hematite, explaining the Cr-rich composition of the studied Bou Azzer hematite (Appendix 3).

Regarding the composition of unaltered chromite cores, both intermediate-Cr and high-Cr chromite overlap the field typical for ophiolitic chromitites (Fig. 7a). The Ti content (Fig. 9a) is similar for the two types of chromite and relatively low when compared with other high-Cr (Cr\(^\#\) >0.6) ophiolitic chromitites (González-Jiménez et al., 2014a, 2017a and references therein), ruling out the addition of Ti during metamorphism noted in other greenstreak to amphibolite facies metamorphosed ophiolitic chromitites (e.g., Colás et al., 2014;
González-Jiménez et al., 2015a and references therein). Trace elements contents in intermediate-Cr and high-Cr chromite cores are within the range for primary igneous chromite (Fig. 9), suggesting that the primary chromite composition is preserved and that high-Cr chromitites are not the alteration product after intermediate-Cr chromitites, allowing petrogenetic interpretations related to the formation of the deposits (see below). Altered chromite rims exhibits the typical Ni V, Zn, and Mn enrichment at ppm levels (Appendix 5) related to the formation of Cr and Fe\(^{3+}\)-rich porous chromite (Colás et al., 2019 and references therein). MORB-normalized trace element patterns of unaltered intermediate-Cr and high-Cr chromite are very similar to those of chromitites from the oceanic supra-subduction zone (SSZ) mantle, in particular to fore-arc chromitites (Fig. 12), suggesting that the minor and trace elements contents in the unaltered chromite cores represent the magmatic fingerprint of a fore-arc environment.

5.2. Parental magma compositions

In the Cr\# versus Mg\# and Cr\# versus TiO\(_2\) plots (Fig. 7b-c), the composition of the Bou Azzer intermediate-Cr chromite falls between the fields defined by Cr-spinel in boninites and mid-oceanic ridge basalts (MORB). In contrast, the composition of the high-Cr chromite plots within the field defined by Cr-spinel in boninites. Using the Al\(_2\)O\(_3\) and the TiO\(_2\) compositions of unaltered chromite cores (Appendix 3), we have estimated the composition of the corresponding melts in equilibrium using the equations for chromite with Cr\#>0.6 by Kamenetsky et al. (2001) modified by Rollinson (2008) for Al\(_2\)O\(_3\) and by Zaccarini et al. (2011) for the TiO\(_2\) content. The Al\(_2\)O\(_3\) contents were estimated with the equation (Al\(_2\)O\(_3\))\(_{\text{melt}}\) = 4.6455 \(\times\) ln(Al\(_2\)O\(_3\))\(_{\text{spinel}}\) - 0.3616, while TiO\(_2\) contents were estimated with the expression

\[
\text{TiO}_2\text{ totals} = 0.089. \quad \text{FeO/MgO ratios were estimated using the Maurel and Maurel's (1982) empirical expression: } \ln(\text{FeO/MgO})_{\text{spinel}} = 0.47 - 1.07\text{Al}^\#_{\text{spinel}} + 0.64\text{Fe}^{3+}\#_{\text{spinel}} - \ln(\text{FeO/MgO})_{\text{melt}}, \text{with FeO and MgO in wt.%}, \text{Al}^\#_{\text{spinel}} = \text{Al}/(\text{Cr} + \text{Al} + \text{Fe}^{3+}), \text{and Fe}^{3+}\#_{\text{spinel}} = \text{Fe}^{3+}/(\text{Cr} + \text{Al} + \text{Fe}^{3+}).
\]

As expected, we have identified two different parental melts for the two types of studied chromitites (Fig. 13). Intermediate-Cr chromitites yield average 12.87 wt% of Al\(_2\)O\(_3\), 0.16 wt% of TiO\(_2\) and 0.90 FeO/MgO ratio, which is similar to MORB melts in terms of Al\(_2\)O\(_3\) content (Fig. 13a; e.g., Gale et al., 2013) but not in terms of TiO\(_2\) (Fig. 13b; typical MORB 1.68 wt% TiO\(_2\); Gale et al., 2013). The low Ti content in MORB-akin melts, together with low Ti/V and Yb/V ratios, is characteristic of fore-arc basalts (FAB; Reagan et al., 2010). According to Shervais et al. (2019), FAB involve a more depleted source than NMORB source mantle, usually recording up to 23% melting. On the other hand, high-Cr chromitites yield average 9.69 wt% of Al\(_2\)O\(_3\), 0.16 wt% of TiO\(_2\) and 1.08 FeO/MgO ratio, corresponding to typical boninitic parental melt compositions (Fig. 13c; e.g., Hickey and Frey, 1982; Dick and Bullen, 1984; Kelemen et al., 2004). The PGE contents in the intermediate-Cr and high-Cr chromitites are similar (Fig. 10a) despite having formed after two different parental melts. This feature could either indicate that these melts originated from the same source (e.g., Zaccarini et al., 2011; González-Jiménez et al., 2015a) or could be the result of higher degree of partial melting (than for typical MORB) in the depleted mantle that originated the FAB melts that formed the intermediate-Cr chromitites (e.g., Shervais et al., 2019).

5.3. PGE signature and PGM formation

The distribution of PGE in the upper mantle is mainly controlled by
Fig. 9. Variations in terms of Ti, Ni, V, Co, Zn, Mn, Sc, and Ga vs. Cr# [Cr/(Cr + Al)] in the Bou Azzer chromite. Fields are from González-Jiménez et al. (2017a) and references therein.
triggers the crystallization of nano-nuggets of IPGE at the chromite rims (Mungall, 2005; Gervilla et al., 2005; Finnigan et al., 2008; Gonzalez Jimenez et al., 2014a, 2014b). According to O’Driscoll and Gonzalez-Jimenez (2016), chromite and IPGE nuggets crystallize most likely from S-un saturated melts with low $f_{O_2}$ in supra-subduction environments. Experimental works (Brenan and Andrews, 2001; Andrews and Brenan, 2002; Bockrath et al., 2004a,b) demonstrated that Os-free laurite precipitates in equilibrium with Os-Ir alloys at the T-$S_f$-$O_2$-$P$ conditions predominating during chromite formation in the upper mantle. Therefore, the Bou Azzer Os-poor laurite grains (Os content between 1 and 6 at.%) would have crystallized contemporaneously with the Os-Ir alloys, as indicated by petrographic observations.

Metamorphism, serpentinization and hydrothermal alteration in the Bou Azzer ophiolitic sequence triggered the destabilization and modification of the primary PGM assemblage. One of the first modifications is the segregation of IPGE nanoparticles from primary laurite grains (Garuti and Zaccarini, 1997; Jimenez-Franco et al., 2020 and references therein). Another modification of the primary PGM assemblage is the formation of secondary Ir-As-S phases, which have only been found as spongy envelopes around Os-Ir alloys (Fig. 5e; Appendix 8c) or coexisting with chloride (Fig. 5f). The formation of these secondary phases requires an increase in the $a_{As}$ of the system (e.g., Thalhammer et al., 1990; Malitch et al., 2001; Gonzalez-Jimenez et al., 2010, 2012), which could be caused by post-serpentinization Cl-rich hydrothermal fluids that circulated in the Bou Azzer area between 380 and 240 Ma (Gasquet et al., 2005; Hodel et al., 2017).

The dunites hosting the Bou Azzer chromitites have PGE contents
(3–30 ppb) much lower than previously reported (22–53 ppb, Ahmed et al., 2009). The chondrite-normalized patterns are generally flat, except for Ru positive anomalies (Fig. 10b). When compared to ophiolitic dunites elsewhere, the PGE contents in the studied dunites are remarkably low and the chondrite-normalized patterns also differ due to the Ru positive anomaly (e.g., Barnes et al., 1985; Leblanc, 1981; Lorand et al., 1999; Ahmed and Arai, 2002; Proenza et al., 2004). Previous studies of PGE in the Bou Azzer serpentinized peridotites also reported positive Ru-Rh anomalies (Ahmed et al., 2009). These authors found that the chondrite-normalized PGE patterns for dunites were similar to the ones corresponding to Co-Ni-Fe-bearing arsenides. Therefore, these Ru-Rh anomalies were explained after the presence of disseminated arsenides in dunites (Ahmed et al., 2009). The low PGE contents of dunites, lower than in spatially related harzburgites (40–68 ppb PGE in Bou Azzer harzburgites; Ahmed et al., 2009) may indicate very strong leaching in dunites. The presence of disseminated arsenides also supports intense fluid circulation in the studied serpentinites. Such leaching could have been a key process regarding the formation of PGE mineralization, such as the Au-Pd deposit of Bleida Far West in the south-eastern part of the Bou Azzer inlier (El Ghorfi et al., 2006).

5.4. Origin and significance of unusual (“exotic”) mineral assemblages

Unusual minerals distinguished in situ in chromite include oriented clinopyroxene lamellae and polymnerallic inclusions of diaspore, hematite and clinohlore. Other minerals identified in the mineral concentrates include moissanite, native Cu and zircon grains with apatite or serpentinite inclusions (Fig. 6). Several of these unusual mineral phases have been commonly interpreted as indicators of UHP conditions and sourced from the mantle transition zone in many ophiolitic rocks worldwide (Table 1), but such models have been challenged by recent studies (Pujol-Solà et al., 2018, 2020a; Farré-de-Pablo et al., 2019a). The occurrence of similar mixed mineral assemblages of continental crust and super-reduced (SUR) and/or ultra-high pressure (UHP) origin as the ones in Bou Azzer is revised in Table 1.

Studies on high-pressure chromite showed that oriented clinopyroxene lamellae could form as exsolutions, together with coesite, after the CaFe$_2$O$_4$-structured (Ca-ferrite) polymorph of chromite (>12.5 GPa,
Table 2

Comparison of Precambrian ophiolitic chromitites worldwide. Zunhua and Dongwazi (China) data are from Huang et al. (2004), Kusky et al. (2004a) and Kusky et al. (2004b), Santa Luz (Brazil) from Oliveira et al. (2007), Outokumpu (Finland) from Liipo et al. (1995), Liipo (1999), Vuollo et al. (1995) and Peltonen et al. (2008), Miaowan (China) from Peng et al. (2012), Eastern Sayan (Russia) from Khain et al. (2002) and Kiseleva and Zhmodik (2017), Jebel Rahid (Sudan) from Abdel Rahman et al. (1990) and Haldar (1977), Bir Tuluha (Saudi Arabia) from Pallister et al. (1988) and Habtoor et al. (2017), Capâne (Dom Feliciano, Brazil) from Marques et al. (2003), Arena et al. (2018) and Werle et al. (2020), Kenticcha Hill (Ethiopia) from Bonavia et al. (1993) and Yibas et al. (2003), Wadi Al Hwanet (Saudi Arabia) from Pallister et al. (1988) and Ahmed et al. (2012), Bou Azzer (Morocco) from Ikenne et al. (2005), El Ghorfi et al. (2007), Ahmed et al. (2009), Hodel et al. (2020) and the present study, Quatipuru (Brazil) from Paixão et al. (2008), Paixão (2009) and Hodel et al. (2019), South Eastern Egypt Desert from Kroner et al. (1992), Ahmed et al. (2001), Saleh (2006), Ahmed (2007), Ahmed (2013), and Hamdy and Lebda (2011), Al’Ays (Saudi Arabia) from Bakor et al. (1976), Pallister et al. (1988) and Prichard et al. (2008), Central Eastern Egypt Desert from Ahmed et al. (2001), Ahmed (2007) and Andresen et al. (2009), Hoggar (Algeria) from Caby (2003) and Augé et al. (2012), Tapo Massif (Peru) from Castroviejo et al. (2009), Tassinari et al. (2011) and Colás et al. (2017), Halaban (Saudi Arabia) from Stacey et al. (1984), Ahmed and Hariri (2001) and Abuamarah (2020), Pampean Ranges (Argentina) from Escayola et al. (2007) and Proenza et al. (2008), Pirapora (Brazil) from Hackschwerder et al. (2000) and Tassinari et al. (2001), and Marlborough (Australia) from Bruce et al. (2000).

| Ophiolite belt       | Country      | Age (Ma) | Orebody length | Chromitite host rock | Textures                  | Geodynamic setting | Cr#       | \(\sum\) PGE(ppb) in chromitites | PGM       |
|----------------------|--------------|----------|----------------|----------------------|--------------------------|--------------------|-----------|--------------------------------|-----------|
| Zunhua & Dongwazi    | China        | 2547 ± 10 | 1-20 m         | Harzburgites         | Disseminated             | SSZ                | 0.88–0.90 | –                               | –         |
|                      |              | Re-Os (TIMS) |                      | Dunites              | Banded                  |                    | –         | –                               | –         |
|                      |              | Model age of chromite from poidiform chromitite |                     |                      | Nodeular                |                    | –         | –                               | –         |
| Santa Luz            | Brazil       | 2085 ± 12 | (minimum age)  | –                    | Serpentinites            | MOR                | 0.60–0.70 | –                               | –         |
|                      |              | U-Pb (SHRIMP) | Zircon from apitite dikes |                     | Harzburgites            |                     | –         | –                               | –         |
| Outokumpu            | Finland      | 1959 ± 5  | 1971 ± 15      | –                    | Harzburgites            | MOR                | 0.59–0.60 | 71–336                          | Laurite Osarsite-Irarsite |
|                      |              | Zircon from gabbros and plagiogranites |                     |                      | Disseminated            |                    | –         | –                               | –         |
| Miaowan              | China        | 1118 ± 24 | 974 ± 11       | –                    | Harzburgites            | SSZ                | –         | –                               | –         |
|                      |              | U-Pb (LA-ICP-MS) | Zircon from gabbros |                     | Dunites                 |                    | –         | –                               | –         |
| Eastern Sayan        | Russia       | 1019 ± 1  | <10 m          | –                    | Dunites                 | SSZ                | 0.59–0.90 | 88–1189                         | Os-Ir-Ru Alloys Laurite Osarsite-Irarsite-Burrunite Hollingworthite (RbAsS) Native Osmium Ir-Ru-Rh sulfoarsenides |
|                      |              | Pb-Pb (TIMS) | Zircon from plagiogranites |                     | Harzburgites            |                    | –         | –                               | –         |
| Jebel Rahid          | Sudan        | 860 ± 17  | ~50 m          | –                    | Dunites                 | SSZ                | 0.85      | –                               | –         |
|                      |              | K-Ar in hornblende | from metagabbros |                     | Harzburgites            |                    | –         | –                               | –         |
|                      |              | 740 ± 15  | K-Ar in metabasalts (whole rock) |                     | Harzburgites            |                    | –         | –                               | –         |
| Bir Tuluha           | Saudi Arabia | 847 ± 14  | 823 ± 11       | 2–10 m               | Dunites                 | SSZ                | 0.72–0.81 | 142–217                         | Laurite |
|                      |              | U-Pb (Two-stage MS) | Model ages of zircon grains from plagiogranites |                     | Harzburgites            |                    | –         | –                               | –         |
| Capané (Dom Feliciano) | Brazil      | 793 ± 0.9 | 757 ± 2.1   | –                    | Serpentinites            | MOR                | –         | –                               | –         |
|                      |              | 715 ± 2.2 | U-Pb (LA-ICP-MS) | Zircon grains from rodeingites |                     |                    | –         | –                               | –         |
|                      |              | ~<30 cm   | Sm-Nd (INAA) Whole-rock age from metavolcanics |                     | Harzburgites            |                    | –         | –                               | –         |
| Kenticha Hill        | Ethiopia     | 789 ± 2.7 | 885 ± 38       | <30 cm               | Serpentinites            | SSZ (FA)           | 0.87–0.91 | 116–205                         | –         |
|                      |              | U-Pb (LA-ICP-MS) | Zircon from metagabbros |                     | Harzburgites            |                    | –         | –                               | –         |
| Wadi Al Hwanet       | Saudi Arabia | 759 ± 2  | ~<5 m          | –                    | Harzburgites            | SSZ (FA)           | 0.60–0.83 | 116–313                         | Laurite Os alloys Irarsite Ir-Os-Ru-Pt-Ni sulfo-arsenide |
|                      |              | U-Pb (Two-stage MS) | Model age of zircon grains from gabbros |                     | Harzburgites            |                    | –         | –                               | –         |
| Bou Azzer            | Morocco      | 780 ± 11  | 5–20 m         | Harzburgites         | SSZ                     | –                   | –         | –                               | –         |
|                      |              | U-Pb (Two-stage MS) | Model age of zircon grains from gabbros |                     | Harzburgites            |                    | –         | –                               | –         |
| Quatipuru            | Brazil       | 759 ± 2  | ~<5 m          | –                    | Harzburgites            | SSZ (FA)           | 0.60–0.83 | 116–313                         | Laurite Os alloys Irarsite Ir-Os-Ru-Pt-Ni sulfo-arsenide |
|                      |              | 1–10 m    | MOR or OCT     | ~0.42–0.61           | 66–176                 | –                   | –         | –                               | –         |

(continued on next page)
phases such as coesite, TiO$_2$-II or cubic-BN (Table 1; Xiong et al., 2017a) have not been identified in the studied thin sections nor in the mineral concentrates. Therefore, we interpret that the oriented clinoxyloxyxene lamellae in the Bou Azzer chromite grains (Fig. 6a-c) did not form after the decompression of the UHP Ca-ferrite polymorph of chromite (cf. Yamamoto et al., 2009). On the other hand, there is no field evidence that the parental melts of the chromitites interacted with silicate melts (i.e. gabbroic rocks; cf. Pujol-Solà et al., 2018, 2020b). Hence, we interpret that these lamellae represent clinoxyloxyxene that crystallized from silicate melt inclusions trapped at the crystallographic planes of the growing chromite grains (Liu et al., 2020). Furthermore, other UHP mineral phases such as coesite, TiO$_2$-II or cubic-BN (Table 1; Xiong et al., 2017a) have not been identified in the studied thin sections nor in the mineral concentrates. Therefore, we interpret that the oriented clinoxyloxyxene lamellae in the Bou Azzer chromite grains (Fig. 6a-c) did not form after the decompression of the UHP Ca-ferrite polymorph of chromite (cf. Yamamoto et al., 2009). On the other hand, there is no field evidence that the parental melts of the chromitites interacted with silicate melts (i.e. gabbroic rocks; cf. Pujol-Solà et al., 2018, 2020b). Hence, we interpret that these lamellae represent clinoxyloxyxene that crystallized from silicate melt inclusions trapped at the crystallographic planes of the growing chromite grains (Liu et al., 2020). Diaspore, associated with hematite and clinochlor, is observed in inclusion trails within the Bou Azzer chromite (Fig. 6d-h). Diaspore is not a common mineral in serpentinized rocks, but it could form under extremely low $a_{SiO_2}$ by desilication of chlorite (Frost and Beard, 2007).
The formation of diaspore may be driven by late seawater infiltration and indicates serpentinization at very low temperature conditions (T < 50 °C; Frost and Beard, 2007). Therefore, the aligned inclusions are interpreted as secondary healed fractures where serpentinization-related fluids circulated (e.g., Farré-de-Pablo et al., 2019a, 2019b; Pujol-Sola et al., 2018, 2020a). Fluid circulation is also evidenced by low hematite (Fig. 4b) and carbonate veins that crosscut the chromitite orebodies. Andradite, formed after the alteration of diopside (Frost and Beard, 2007), has been distinguished in the altered silicate matrix (Appendix 2) and can also be associated with low-T (≤225 °C) serpentinization fluids (Frost and Beard, 2007). These late fluids enriched in Al, Fe³⁺ and Ca may be related to rodingitization of the surrounding mafic rocks, as in the Halaban ophiolite in Saudi Arabia (Abuamarah, 2020) and in the Eastern Desert of Egypt (Mubarak et al., 2020). In Bou Azzer, rodingites are reported in association with silfer mineralization (Leblanc and Loubau, 1988).

SuR phases, including diamond, moissanite and native elements, are quite common in mineral concentrates from ophiolitic chromitites worldwide (Table 1). Globally, these have been interpreted as formed at the mantle transition zone (410-660 km depth; e.g., Lian et al., 2017). However, we interpret that the SuR phases (moissanite and native Cu) recovered in the Bou Azzer mineral concentrates (Fig. 6k) formed during serpentinization processes as there is no evidence of UHP conditions in Bou Azzer. Empirical observations (Pujol-Sola et al., 2018) and thermodynamic calculations (Pujol-Sola et al., 2020a; Ballhaus et al., 2020) indicate that SuR phases can form during serpentinization (350 °C and 100 MPa) in super-reduced microenvironments (inclusions) in which oxygen fugacity can be as low as fO₂ (MPa) = −45.3 (ΔlogfO₂[Iron-Magnetite] = −6.5; Pujol-Sola et al., 2020a).

Zircon grains hosting serpentine inclusions (denoting the former presence of ferro-magnesian minerals, notably olivine; Fig. 6m) recovered from the Bou Azzer chromitites could have crystallized at shallow mantle levels during the formation of the chromitites or during further interaction with silicate melts, as reported in other chromitites (Pujol-Sola et al., 2020b). The presence of apatite inclusions within other recovered zircon grains (Fig. 6l) may however indicate crystallization from a continental crustal magma. These potentially xenocrystic zircon grains may hence be linked to the transference of detrital zircon from subducted sediments to the upper mantle wedge and later encapsulation within chromite (Robinson et al., 2015; Rojas-Agramonte et al., 2016; Gonzalez-Jiménez et al., 2017a; Proenza et al., 2018; Torró et al., 2018). Subduction of WAC (West African Craton)-derived sediments accumulated on top of the subducting oceanic lithosphere ahead the cratons could facilitate the transfer of detrital zircons to the mantle wedge and their incorporation to the chrome-forming magmas.

Overall, we suggest a simple crystallization process for the Bou Azzer chromitites, discarding UHP crystallization (Yang et al., 2014, 2015) or recycling of low-pressure chromitites to great depth via mantle convection (Arai, 2015; Griffin et al., 2016). In contrast, we observe that the unusual mineralogy formed during the serpentinization of the chromitites and the host peridotites, from relatively high temperature conditions forming chlorite, moissanite and native Cu, to lower temperature conditions, forming andradite and diaspore.

5.5. Comparison with other Precambrian ophiolitic chromitites

Precambrian ophiolites are quite common in the geological record, even though in most cases, they are strongly altered, dismembered and characterized as “greenstone belts” (Furnes et al., 2015). Most of these Precambrian ophiolites are subduction-related, generated in fore-arc or back-arc environments (Furnes et al., 2015). Table 2 reports the occurrence of chromitite orebodies within 21 Precambrian ophiolitic sequences of South America, Asia, Africa, Europe, and Australia, together with the studied ophiolitic sequence from Morocco, spanning from 2500 to 560 Ma (see the Table 2 caption for references). When compared to the more abundant Panerhozoic supra-subduction zone
Ophiolites (e.g., Furnes et al., 2015), it is striking the limited number of locations of Precambrian chromitites. In fact, most known economic chromitite deposits are Late Paleozoic to younger (Stowe, 1994; Arai and Ahmed, 2018).

Precambrian chromitites are mostly typically show massive textures and are centimetric to metric in size, with some exceptions such as the chromitites from the Hoggar ophiolite (Algeria) that reach 250 m in length (Augé et al., 2012) and those from the Tapo Massif (Peru) that reach around a hundred meters in length (Castroviejo et al., 2009; Colás et al., 2017) (Table 2). Regarding Cr#, it is highly variable, from 0.37 (Marlborough chromitites, Australia; Bruce et al., 2000) to 0.91 (Kentchica Hill chromitites, Ethiopia; Bonavia et al., 1993), though most orebodies are high-Cr (Cr# > 0.6; Table 2; Fig. 14a). A clear correlation between the composition of the chromitites and the age of the host ophiolite is not observed (Fig. 14a). However, younger chromitites generally have lower Cr# (Cr# < 0.7) than older chromitites (Fig. 14a), as already observed by Arai and Ahmed (2018). In order to establish a potential correlation, and since the compositional information is in many cases partial and the post-magmatic chemical variations are not assessed, further studies on some of these Precambrian ophiolitic chromitites are needed.

The observed range of PGE content in Precambrian chromitites is very large, from 11 ppb (Pampean Ranges, Argentina; Proenza et al., 2008) to 10 ppm (Al‘Ays, Saudi Arabia; Prichard et al., 2008; Table 2), still, most orebodies have 2PGE at ppb levels (Fig. 14b). The observed enrichment in PGE in Al‘Ays chromitites (Saudi Arabia; 131–10463 ppb; Prichard et al., 2008) or in Sayan chromitites (Russia; 88–1189 ppb; Kiseleva and Zhmodik, 2017) is anomalous and could be related to post-magmatic processes such as metamorphism. Laurite is the most important PGM in most chromitites (Table 2), followed by Os alloys and erlichmanite, indicating an enrichment in IPGE regarding PPGE, which is typical in mantle-hosted SSZ chromitites (e.g., González-Jiménez et al., 2014b). Even though a relationship between the Cr# of chromite and the PGE content is typically observed (e.g., González-Jiménez et al., 2014b, we do not observe a clear trend in the reviewed Precambrian chromitites (Fig. 14b). To the authors’ knowledge, mineral associations nominally indicative of UHP or SuR conditions have not been described in the reviewed Precambrian ophiolitic chromitites listed in Table 2, except for the Zunhua Archean chromitites, where Kusky et al. (2019) reported UHP polymorphs of chromite and rutile (TiO₂-II). On the other hand, most chromitites formed in a supra-subduction zone setting, but fore-arc or back-arc locations have not been determined, strengthening the need of further studies on these chromitites.

In terms of Cr# (Fig. 14a), the composition of the studied Bou Azzer chromitites is very similar to Neoproterozoic chromitites from Egypt (e.g., Ahmed, 2007; Ali et al., 2020), Sudan (Abdel Rahman et al., 1990) and Saudi Arabia (e.g., Pallister et al., 1988). The corresponding ophiolitic bodies belong to the Arabian-Nubian shield and are related to the Panafrikan orogeny as much as the Moroccan Anti-Atlas. However, in north-western African ophiolites, chromitites have only been described in Bou Azzer and not in other ophiolites such as the Khzama sequence in the Sirwa inlier (e.g., Hodel et al., 2020; Chaib et al., 2021) and this may be related to the scarcity of chromitites in Precambrian ophiolites as stated above (e.g., Stowe, 1994). In the South American margin of Gondwana, Neoproterozoic ophiolitic chromitites have been reported in Peru (Tapo Massif: 718 Ma; Colás et al., 2017), Brazil (Capané: 793–715 Ma, Quatipuru: 757 Ma, and Pirapora: 628 Ma; Marques et al., 2003; Arena et al., 2018; Paixão et al., 2008; Paixão, 2009; Hodel et al., 2019; Hackspacher et al., 2000; Tassinari et al., 2001) and Argentina (Pampean Ranges: 647 Ma; Proenza et al., 2008). Even though some authors (Paixão et al., 2008) attempted to correlate the Neoproterozoic Araguaia belt in Brazil (Quatipuru ophiolite) with the NW African Mauritanide-Basseride-Rockelide belts, the well-studied ophiolitic chromitites in South America have compositions richer in Al₂O₃ than the Bou Azzer chromitites (Table 2). These differences, coupled with a general lack of geological data regarding the geodynamic
setting of the ophiolites and the Neoproterozoic suture zones, makes it very difficult to relate the South American ophiolites to the Moroccan Bou Azzer ophiolite.

5.6. Geodynamic setting and tectonic implications

Arenas et al. (2020) have recently proposed a geodynamic model for the Neoproterozoic-D Devonian margin of Gondwana in which the generation of accreted oceanic lithosphere seems to occur at 100 Ma intervals, as recorded by the age of obducted Neoproterozoic to Devonian ophiolites in Morocco and Iberia. In this model, all these ophiolites were collectively generated in the supra-subduction per-Gondwana realm during the opening of fore-arc and back-arc basins. Other authors have interpreted the formation of the Bou Azzer ophiolite in an intra-oceanic arc setting (e.g., Gasquet et al., 2005; El Hadi et al., 2010; Walsh et al., 2012; Hodel et al., 2020). However, there is still debate on whether there is one or multiple magmatic arcs (Admou et al., 2013; Soulaimani et al., 2018; Triantafyllou et al., 2018, 2020) and whether the ophiolite formed in a fore-arc (e.g., Saquaque et al., 1989; Naidoo et al., 1991; Ahmed et al., 2005; El Hadi et al., 2010; Walsh et al., 2012; Arenas et al., 2020) or a back-arc setting (e.g., Bodinier et al., 1984; Triantafyllou et al., 2018; Hodel et al., 2020).

The composition of unaltered chromite cores from the Bou Azzer chromitites reveals the presence of two compositional groups of chromitites: intermediate-Cr (Cr# = 0.60–0.74) and high-Cr (Cr# = 0.79–0.84) chromitites (Fig. 7). This distinction was not reported in previous studies of the Bou Azzer chromitites (e.g., Ikenne et al., 2005; El Ghorfi et al., 2007; Ahmed et al., 2009) but it is highly relevant because it translates into two types of parental melts for the studied chromitites. Intermediate-Cr chromitites yield parental melts similar to MORB but with lower TiO₂ contents (the low Ti content in the chromites is also observed in the trace elements in Fig. 9a) corresponding to FAB melts, whereas high-Cr chromitites yield boninitic parental melts. This association of melts only occurs in fore-arc regions during subduction-initiation (Reagan et al., 2010; Whattam and Stern, 2011; Torró et al., 2017; Shervais et al., 2019; Liu et al., 2019; Pandey et al., 2019; Whattam et al., 2020). In this setting, extension of the upper plate due to rollback of the sinking plate contributes to a stronger interaction of the mantle flowing to the nascent mantle wedge with fluids from the subducting plate, triggering a higher degree of melting, which is translated into a depletion of Ti, and possibly into an increase in the PGE content in the released melts when compared to typical MORB (Reagan et al., 2010; Shervais et al., 2019). In the Izú-Bonín Mariana (IBM) fore-arc, FAB occur stratigraphically below and <2 Ma older than the associated boninite sequence (Reagan et al., 2010, 2013). In Bou Azzer, intense deformation, alteration and metamorphism obscure the stratigraphy of the volcanic sequence.

Trace elements contents in the studied unaltered chromite cores show patterns very similar to fore-arc chromitites (Fig. 12). Additionally, the magmatic rocks that form the Bou Azzer ophiolitic crustal sequence (gabroic rocks and undifferentiated volcanic rocks and dikes) show characteristics of a subduction-initiation ophiolite formed in a fore-arc environment (Arenas et al., 2020). Therefore, the origin of the Bou Azzer chromitites is conceptualized within a subduction-initiation ophiolite model (Whattam and Stern, 2011). In this context, chromitites formed in the fore-arc during the early stages of a Neoproterozoic intra-oceanic arc developed ahead the West African Craton margin. Similar studies have also interpreted the formation of chromitite bodies with different compositions in a subduction-initiation geodynamic setting (e.g., Moghadam et al., 2015; Zhang et al., 2015b; 2016, 2020; Uysal et al., 2018). According to the subduction-initiation model, from early to more mature stages of subduction, melts evolve from FAB to boninites and island arc tholeiites to calc-alkaline arc magmas (Reagan et al., 2010; Whattam and Stern, 2011; Ishizuka et al., 2014; Shervais et al., 2019; Whattam et al., 2020). In this setting, during early stages of intra-oceanic subduction (Fig. 15a) intermediate-Cr chromitites formed from FAB melts that were generated by initial spreading of oceanic crust and melting of the nascent mantle wedge. At this stage, there is little or no mass transfer from the subducting slab (Fig. 15a; Liu et al., 2019). Later, as subduction proceeded, high-Cr chromitites precipitated from hydrated melts with boninitic affinity that migrate through the mantle wedge in the fore-arc (Fig. 15b; e.g., Shervais, 2001; Dilek and Furnes, 2014; Moghadam et al., 2015).

Our interpretation of the geodynamic setting of formation of the Bou Azzer ophiolite in the fore-arc clearly differs from the recent proposal of a back-arc SSZ setting by Hodel et al. (2020). In the studied North Ait Ahmane ophiolitic sequence (Fig. 1), high-Cr chromitites (Filon 60 de- posits) are located in between chromitites with intermediate-Cr composition (Igoujim and Ait Ahmane deposits). This interesting feature can be related to imbrication of the ophiolitic sequence during the obduction onto the WAC passive margin (El Hadi et al., 2010), hence repeating the serpentinized harzburgite sequence as suggested by Arenas et al. (2020) based on its unusual thickness.

6. Concluding remarks

We interpret that the Bou Azzer chromitites formed in a subduction-initiation geodynamic setting with two-stages of evolution, including formation of intermediate-Cr chromitites from fore-arc basalts (FAB) in the early stage and formation of high-Cr chromitites from boninitic melts in the ensuing stage. The studied chromitites are enriched in IPGE with respect to PPGE as observed in the magmatic PGM: Os-poor laurite and Os-Ir alloys. Unusual mineral phases in the studied chromite grains include clinoxyropene lamellae, moissanite, native Cu, diaspore, and zircon, and these were formed during shallow magmatic crystallization or via different stages of post-magmatic alteration related to serpentinitization, rather than having UHP origin. Precambrian ophiolitic chromitites are quite rare compared to Phanerozoic ophiolitic chromitites and tend to be richer in Cr, while the PGE content is highly variable and clear trends related to the ophiolites age cannot be defined. The studied chromitites are very similar to Neoproterozoic ophiolitic chromitites of the Arabian-Nubian shield, also related to the Panafricane orogeny.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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