Precambrian Research 300 (2017) 151–167

Contents lists available at ScienceDirect

Precambrian Research

journal homepage: www.elsevier.com/locate/precamres

# Unusual massive magnetite veins and highly altered Cr-spinels as relics of a Cl-rich acidic hydrothermal event in Neoproterozoic serpentinites (Bou Azzer ophiolite, Anti-Atlas, Morocco)

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ARTICLE INFO

*Keywords:*
Neoproterozoic
Serpentinite
Hydrothermalism
Magnetite
Cr-Spinel
Ophiolite

ABSTRACT

If magnetite is a common serpentinization product, centimetric, massive and pure magnetite veins are rarely observed in serpentinites. Unique example, in the Aït Ahmane ultramafic unit (Bou Azzer Neoproterozoic ophiolite, Anti-Atlas, Morocco) allows to assess the hydrothermal processes that prevailed at the ending Precambrian. In this study, rock magnetism, petrography, mineral and bulk chemistry are combined to assess iron behavior in these meta-ultramafics, in order to constrain the serpentinites alteration and magnetite veins formation processes.

Very high Cr#, low Mg#, high $Fe^{3+}$# and low Ti content of Cr-spinels cores reflect a supra-subduction zone origin for the Aït Ahmane serpentinites precursor. Typical lizardite/chrysotile pseudomorphic texture in fresh serpentinites reveals an initial oceanic-like serpentinization, involving temperature < 350 °C while the abundance of magnetite (up to 10.14 wt%) in these unaltered serpentinites attests of a relatively high serpentinization temperature > 200 °C. Magnetic measurements reveal a lower magnetite content in hydrothermalized serpentinites hosting the magnetite veins, with lowest values (down to 0.58 wt%) for bleached serpentinites constituting the wall rock of the veins. These magnetic data are consistent with bulk rock chemistry showing a lower total iron content in hydrothermalized serpentinites. Hysteresis parameters and thermomagnetic measurements denote a magnetic grains size that increases with the alteration, associated with the emergence of a new magnetic phase (Cr-magnetite) produced by Cr-spinels alteration. A new proxy, based on thermomagnetic measurements, the CrM/M ratio, provides a quantification of its contribution to the magnetic susceptibility. Mineral chemistry allowed to identify the Cr-spinels alteration sequence and reveals an important chlorine enrichment in serpentine phases from hydrothermalized serpentinites.

These results suggest that a Cl-rich acidic hydrothermal event involving temperatures below 350 °C produced an intense magnetite leaching in the host serpentinite and an advanced Cr-spinels alteration to ferritchromite and Cr-magnetite. Iron provided by this leaching have led to the formation of unique magnetite veins in the Aït Ahmane ultramafic unit. Two different settings are proposed for the hydrothermal event: (1) a continental hydrothermal system as advanced for the Co-Ni-As ores in the Bou Azzer inlier or (2) an oceanic black smoker type hydrothermal vent field on the Neoproterozoic seafloor.

## 1. Introduction

Precambrian ophiolites (see a compilation in Furnes et al., 2015) are the only remains of the ancient oceanic lithosphere and related metamorphic and hydrothermal processes affecting it, such as serpentinization (e.g. O'Hanley, 1996; Mével, 2003). If the geodynamical context in the Neoproterozoic such as the presence and subsequent dislocation of Rodinia supercontinent have been evoked to explain the

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http://dx.doi.org/10.1016/j.precamres.2017.08.005
Received 10 March 2017; Received in revised form 11 July 2017; Accepted 5 August 2017
Available online 12 August 2017

occurrence of global glaciations and the second rise of oxygen (Donnadieu et al., 2004; Macouin et al., 2015; Gernon et al., 2016; Lee et al., 2016), the contribution of ocean-floor formation and hydrothermal processes to the drastic changes of the geo-biosphere occurring during this time period received little attention.

Serpentinization and associated hydrothermal alteration processes have shown their influence on the geo-biosphere, notably by their relation to carbon sequestration (e.g., Seifritz, 1990; Lackner et al., 1995; Kelemen and Matter, 2008), $H_2$ production and life emergence (Corliss et al., 1981; Charlou et al., 2002; Früh-Green et al., 2004; Sleep et al., 2004; Kelley et al., 2005; Russell and Arndt, 2005; McCollom and Bach, 2009; Evans, 2010; Muntener, 2010; Ménez et al., 2012). In the same way, hydrothermal vents are often evoked as a habitat for ecosystems as well as iron providers, especially during the Precambrian (e.g. Kump and Seyfried, 2005). Hydrothermal vents have been also advanced in some hypothesis related to banded-iron formations deposition (Kump and Seyfried, 2005; Johnson et al., 2008; Yanhe et al., 2014). Both serpentinization and hydrothermal activity appear to play an important role in the iron cycle. Indeed, magnetite ($Fe_30_4$) is a notable serpentinization product (Toft et al., 1990; Oufi et al., 2002; Bach et al., 2006; Beard et al., 2009; Klein et al., 2009, 2014; Evans, 2010; Maffione et al., 2014; Bonnemains et al., 2016), and its abundance can provide constrains on temperature and $H_2$ production (Seyfried et al., 2007; Klein et al., 2009, 2014; Malvoisin et al., 2012a, 2012b; Bonnemains et al., 2016). During serpentinization, magnetite first crystallized in the serpentine mesh rims following iron oxidation related to olivine serpentinization (e.g., Klein et al., 2009; McCollom and Bach, 2009; Rouméjon et al., 2015). Small grains of magnetite ($< 1$ μm) outline serpentinizing microfractures and generally concentrate to form a polygonal pattern surrounding the mesh cells (e.g. Rouméjon et al., 2015). Volume increase due to serpentinization could also open fractures where serpentine and/or brucite precipitate in association with magnetite forming microveins (Andreani et al., 2007; Beard et al., 2009).

If magnetite is ubiquitous in serpentinized peridotites, major serpentinites hosted magnetite ores are rare. The only exploited one in the world is the Cogne magnetite ore (Aosta Valley, Western Italian Alps). Carbonin et al. (2015) described the mineral associations of Cogne, including serpentinites rich in magnetite (79.1 wt% $FeO_{tot}$), calcite, andradite/hydroandradite and diopside, as a product of Ca metasomatism at 300–360 °C conveyed by C-O-H saturated fluids. They evoked a fluid/rock interaction on the Tethyian seafloor in a hydrothermal vent field setting.

In this study, we focus on unique pluri-centimetric and massive magnetite veins in the Neoproterozoic Aït Ahmane serpentinized peridotites, part of the Bou Azzer Neoproterozoic ophiolite (Moroccan Anti-Atlas; Leblanc, 1975; Gahlan et al., 2006; Ahmed et al., 2009a, 2009b), in order to identify a possible hydrothermal origin for the magnetite veins. To investigate this ultramafic unit, we used magnetic methods that have proven their potential to track magnetite in serpentinized ultramafics (Toft et al., 1990; Oufi et al., 2002; Bach et al., 2006; Malvoisin et al., 2012b; Maffione et al., 2014; Bonnemains et al., 2016; Fujii et al., 2016a). These results are combined with mineral chemistry and petrographical observations to constrain the formation processes of magnetite veins as well as the nature of the associated fluid. The study of such unusual massive magnetite veins provides new insights in the geological setting and the type of hydrothermalism associated to the evolution of the Neoproterozoic exhumed lithospheric mantle.

## 2. Geological setting and sampling

The Aït Ahmane ultramafic unit is located in the Bou Azzer-El Graara Window (also called the Bou Azzer inlier) and belongs to the central part of the Anti-Atlas orogenic belt, in southern Morocco, between the High-Atlas Mountains to the north and the Sahara desert to the south. It consists in a Pan African orogenic belt along the northern edge of the Eburnean West African Craton (WAC), (Fig. 1.a).

Anti-Atlas Precambrian basements are exposed in several inliers (e.g., Bou-Azzer, Zenaga, Sirwa, Saghro) along two major fault zones: the South Atlas Fault and the Anti-Atlas Major Fault (Gasquet et al., 2005). The Bou Azzer inlier forms a 60 × 10 km depression, made of several stacked tectonic blocks interpreted as dismembered parts of a Neoproterozoic oceanic supra-subduction zone system (e.g. Saquaque et al., 1989; Hefferan et al., 2002; Bousquet et al., 2008). These units are moulded along the Anti-Atlas Major Fault (AAMF; Fig. 1.b), surrounded and locally topped by unconformable Ediacaran volcano-clastic deposits of the Ouarzazate Supergroup and late Ediacaran to Early Cambrian clastic sediments (Leblanc, 1981). The Bou Azzer inlier consists in (Fig. 1.c):

(i) A highly tectonized ophiolitic assemblage forming the core of the Bou Azzer inlier. It mainly comprises upper-mantle peridotites (including Aït Ahmane ultramafic unit studied here), mafic and ultramafic metacumulates (e.g. metapyroxenite, layered metagabbro), mafic dykes swarm, meta-basaltic sheeted dykes, pillow lavas in a smaller extent and associated volcano-sedimentary sequences (Leblanc, 1975, 1981; Bodinier et al., 1984; Naidoo et al., 1991; Hefferan et al., 2002; Gasquet et al., 2005, 2008; Bousquet et al., 2008).
(ii) Several polymetamorphic complexes (760–690 Ma) cropping out to the south and the north of the ophiolitic sequence. These are made of basic to acid metavolcanic rocks (i.e. the Tichibanine-Ben Lgrad complex) and metaplutonic units (i.e. the Bougmane complex; D'lemos et al., 2006; Blein et al., 2014; Triantafyllou, 2016).
(iii) Intrusive syn-tectonic dioritic to granodioritic plutons that mainly crosscut the ophiolitic units. Their emplacements were dated (U-Pb on zircons) between 660 and 640 Ma (Inglis et al., 2005; El Hadi et al., 2010; Walsh et al., 2012; Blein et al., 2014).

The Aït Ahmane ultramafic unit is located in the central part of the Bou Azzer inlier and represents the mantle section of the ophiolitic sequence (Fig. 1.c). Although extensive literature exists on this Proterozoic ophiolite, its age and geodynamic evolution remains unclear and debated. It was first considered as remnants of oceanic lithosphere by Leblanc (1975). The first geochemical data obtained on the metabasalts (Bodinier et al., 1984) pointed to a back-arc setting (formerly referred as marginal basin) while more recent analyses were interpreted as a fore-arc signature (Naidoo et al., 1991; Ahmed et al. 2005; Ahmed et al., 2009a,b). A 697 Ma age has been published for this ophiolite (El Hadi et al., 2010) but the sample dated by these authors is a garnet-bearing metagabbro that belongs to the lower crust of the southern Bougmane arc complex (Triantafyllou, 2016). To date, the only valid age for ophiolitic rocks from the Anti-Atlas belt has been obtained by Samson et al. (2004) on a very similar ophiolitic complex in the Sirwa window where U-Pb zircon dating on plagiogranite yielded an age of 762 Ma.

The Bou Azzer ophiolite is also well known for Co-Ni-As (± Ag ± Au) deposits that are often found near the contact between the 660 and 640 Ma diorites and the ophiolitic serpentinites. Radiometric dating and geological field arguments suggest that the ophiolite was subjected to several hydrothermal alteration phases of between the Cambrian and the Triassic (Bouabdellah et al., 2016 and references therein).

The Aït Ahmane ultramafic unit is dominated by fully or almost fully serpentinized harzburgites, disseminated dunite lenses and chromite pods. The largest serpentinite outcrop is located next to the Aït Ahmane locality. It hosts, metric to decametric hydrothermally altered circulation zones containing pluri-centimetric wide stout and fibrous magnetite veins (Leblanc, 1975; Gahlan et al., 2006; Fig. 2.a).

Samples were collected in this area (Fig. 1.c). Below, the terms hydrothermally altered serpentinites and dark fresh serpentinites will respectively refer to altered serpentinites from these circulation zones and the unaffected or weakly affected ones respectively.