Lithos 228–229 (2015) 78–89

Contents lists available at ScienceDirect

Lithos

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

Fluid-present deformation aids chemical modification of chromite: Insights from chromites from Golyamo Kamenyane, SE Bulgaria

Takako Satsukawa [a,*], Sandra Piazolo [a], José María González-Jiménez [a,b], Vanessa Colás [a,c], William L. Griffin [a], Suzanne Y. O'Reilly [a], Fernando Gervilla [d], Isabel Fanlo [c], Thomas N. Kerestedjian [e]

[a] Australian Research Council Centre of Excellence for Core to Crust Fluid Systems/GEMOC, Department of Earth and Planetary Sciences, Macquarie University, Sydney, NSW 2109, Australia
[b] Departamento de Geología and Andean Geothermal Center of Excellence (CEGA), Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile
[c] Departamento de Ciencias de la Tierra, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain
[d] Departamento de Mineralogía y Petrología and Instituto Andaluz de Ciencias de la Tierra, Universidad de Granada-CSIC, Avda. Fuentenueva s/n, 18002 Granada, Spain
[e] Geological Institute, Bulgarian Academy of Sciences, 24 Georgi Bonchev Str., 1113 Sofia, Bulgaria

ARTICLE INFO

Article history:
Received 28 November 2014
Accepted 25 April 2015
Available online 9 May 2015

Keywords:
Chromite
Crystal-plastic deformation
Chromite recrystallization
Metamorphic modification
Fluid present deformation

ABSTRACT

Chemical signatures of chromitites are commonly used to track the evolution of the Earth's mantle. However, chemical modification during deformation may have important implications for the interpretation of chromites' signatures. Here, we describe the details of how deformation promotes chemical modification in chromite. Physicochemical characteristics of the chromites were quantified by measuring crystallographic orientation relationships using Electron Back-Scattered Diffraction (EBSD) and electron microprobe analysis (EMP). Chromites show porphyroclastic textures with coarse-grained porphyroclasts (ca. 0.2–5 mm) and fine-grained neoblasts ($<$200 μm). Coarse-grained chromites are chemically zoned in terms of major elements from core to rim, preserving this initial igneous feature in the cores, while the outer rims reveal a metamorphic signature. Large chromite grains are characterized by local crystal-plastic deformation, exhibiting distinct inter-crystalline deformation including continuous crystal bending and subgrain boundaries as well as chemical modification in their outer, deformed parts. Two types of fine-grained chromite, F1 and F2, are present. While F1 exhibits a well-developed polygonal texture, straight grain boundaries and low intercrystal misorientation ($<$1°), F2 shows low-angle boundaries and significant intercrystalline misorientation (2–8°). Both F1 and F2 have higher Fe^{3+} and Cr and lower Mg# values than the cores of large grains. We interpret F1 and F2 to represent chromite recrystallized by heterogeneous nucleation and subgrain rotation recrystallization, respectively. Crystallographic preferred orientation (CPO) and misorientation data on the well-developed low-angle (subgrain) boundaries in coarse grains and F2 grains indicate that deformation in chromite was accommodated mainly by dislocation creep with the dominant activation of the {111}<100> slip system. The retrograde P–T exhumation path predicted by thermodynamic and chemical modeling suggests that these fine-grained chromites were produced when the initial chromitites reacted with oxidizing fluids during retrograde metamorphism (~1.0 GPa and 500–700 °C). Our results show that deformation in the dislocation-creep regime in a chemically open system has induced chemical modification and homogenization within chromite aggregates as well as strain localization. This close physicochemical link offers new avenues of interpreting the chemical signatures of chromites, utilizing their microstructurally controlled variation or lack thereof.

1. Introduction

Chromite is one of the main reservoirs of chromium in the Earth (e.g. Arai, 1992, 1997; Barnes and Roeder, 2001; Stowe, 1994). It is an essential phase in the mineral assemblage of the upper mantle peridotites preserved in ophiolites, where it can be concentrated in bodies known as chromitites (e.g., González-Jiménez et al., 2014). Scientific interest in chromite arises from the fact that within peridotitic rocks, chromites in general are better preserved than silicates, as they are more resistant to fluid-related processes; this has led to the widespread use of chromitites to track the evolution of the Earth's mantle convection (e.g. Arai, 2010; González-Jiménez et al., 2012, 2014; Miura et al., 2012; Walker et al., 2002). Chromitites in ophiolites are commonly hosted within discordant or subconcordant dunite bodies, within the shallow mantle part of the oceanic lithosphere (e.g. Arai and Abe, 1995; Arai and Yurimoto, 1994; Gervilla et al., 2005; González-Jiménez et al., 2014; Melcher et al., 1997; Proenza et al., 1999; Zhou et al., 1994, 1996).

A global chromitite cycle from crust to mantle and back again has been suggested by geochemical studies (Arai, 2013; McGowan et al.,

---

* Corresponding author. Tel.: +61 2 9850 8346; fax: +61 2 9850 8943.
E-mail address: takako.satsukawa@mq.edu.au (T. Satsukawa).

http://dx.doi.org/10.1016/j.lithos.2015.04.020
0024-4937/© 2015 Elsevier B.V. All rights reserved.

2015, and references therein). Utilizing chemical signatures without direct investigation of the possible deformation features may result in a biased interpretation, as it has been demonstrated for other minerals that the chemical signature may be significantly influenced by deformation (e.g. Büttner, 2005; Erickson et al., 2015; Kruse and Stünitz, 1999; McCaig et al., 2007; Pearce and Wheeler, 2010; Timms et al., 2006). Hence, for improved interpretation and a realistic understanding of the various chemical signatures commonly observed in metamorphosed chromites, it is crucial to understand in depth the link between chemical signature and deformation. However, the assessment of the deformation mechanisms affecting chromite chemical signatures has been hampered, because such a study requires us to distinguish grains and subgrains, to quantify the preferred orientation of chromite, and to link chemical changes to these crystallographic relationships. Because chromite is isotropic, it has been difficult to derive crystallographic relationships in chromite aggregates via optical microscopy.

With the advent of advanced microanalytical techniques, it is now possible to study deformation of chromite in detail; detailed analysis of orientation relationships can be achieved through Electron Back-Scattered Diffraction (EBSD) analysis (Prior et al., 1999). Recently, the EBSD technique has been used to study chromite crystallographic relationships (Prichard et al., 2015; Vukmanovic et al., 2013); neither of these studies has discussed the details of possible deformation processes. Besides the potential influence of deformation on chemical signatures, the identification and characterization of deformation mechanisms in chromite-rich zones are of interest because these mechanisms govern the rheological response of chromite-dominated rocks (e.g. Frost and Ashby, 1982). Deformation mechanisms such as plastic deformation including diffusion creep (Christiansen, 1985; Ozawa, 1989), dissolution followed by precipitation in the presence of melt, and/or dislocation creep (Secher, 1981) are expected to play a role in the modification of chromite microstructures, but have so far commonly been overlooked due to the analytical problem noted above.

Dislocation creep is not thought to be a dominant mechanism; instead, diffusional creep, which normally does not produce an oriented crystallographic fabric, was considered to be the principal mechanism in the deformation of chromites (Ozawa, 1989). In deformed ophiolitic chromitites, large grains are commonly perfect without bending of the lattice or internal substructures (e.g. subgrains), and no crystallographic preferred orientation of chromite has been detected using the X-ray goniometer (Christiansen, 1985). These features have been interpreted to indicate that chromite mainly deforms by passive rotation in the weaker silicate matrix, and by cataclasis and/or diffusion creep (Christiansen, 1985).

However, microstructural work on chromites in ophiolites from Oman, Vourinos (Greece) and Tiebaghi (New Caledonia) (Christiansen, 1986) utilizing electron channeling patterns in scanning electron microscope (SEM) showed that dislocation creep is active in chromite deformed at high temperatures under mantle conditions. Nevertheless, Christiansen (1986) implied that diffusion-accommodated flow is significant and mechanisms related to dislocation structures only provide a secondary mode of deformation compared to brittle fracturing and passive rotation of chromite grains and fragments in the weaker (silicate) matrix.

Few other studies have investigated the deformation of chromite in chromitites (Ghosh and Konar, 2012; Ghosh et al., 2014; Huang et al., 2004), and these were limited to microscopic observations of the transition from brittle to crystal-plastic flow. Recent observations from back-scattered electron (BSE) images obtained using SEM as well as electron microprobe (EPMA) have identified substructures in ophiolitic chromitites, and suggest that in general dislocation processes may be active in chromite deforming at high temperatures during mantle flow (Ghosh et al., 2013, 2014). However, these authors did not provide the required key detailed orientation data and information on slip system activation.

This paper presents an EBSD study combined with chemical mapping and spot analysis of natural chromite samples from chromitites hosted in the serpentinite body of Golyamo Kamenyane, in south Bulgaria (Colás et al., 2014; Gervilla et al., 2012). These chromitites have undergone deformation concomitant to fluid–rock interaction during metamorphism, and previous work suggested that these chromitites are one of the most chemically modified and deformed examples (Colás et al., 2014). We document how chromite has deformed under fluid-present amphibolite-facies conditions, providing new insights into the microstructural evolution of chromite during retrograde metamorphism. The results show how, during deformation, the chemical signature of chromite is markedly modified, suggesting that studies utilizing chromite chemistry to infer conditions at high PT and a specific chemical environment need to take into account the effects of deformation on the chemical signature.

2. Geological setting and samples

The studied chromitites are enclosed in serpentinized peridotites of the Golyamo Kamenyane massif, which is part of a dismembered ophiolite complex in the upper unit of the metamorphic basement of the Eastern Rhodopes crystalline massif in southern Bulgaria (Bonev, 2006; Haydoutov et al., 2004; Kolcheva et al., 2000) (Fig. 1). According to recent investigations, the ultramafic rocks of the Eastern Rhodopes have undergone ultra-high pressure (UHP)/high temperature (HT) metamorphism (>2.5 GPa and >1200 °C), and a later overprint at eclogite- or granulite-facies (1.4–1.6 GPa and 750–775 °C). A later amphibolite-facies (~1.0 GPa and 600–650 °C) overprint is also recorded in metasediments spatially associated with the mantle rocks (e.g. Mposkos and Krohe, 2006; Mposkos, 2002). Mposkos et al. (2011) have estimated a similar retrograde metamorphic pathway in the rocks of the adjacent Gneiss Migmatite Complex: from ultra-high pressure (2.1–2.3 GPa) with lower temperatures (533–617 °C), to eclogite-facies (1.5–1.9 GPa and 566–672 °C) and then an amphibolite-facies overprint (0.7–0.9 GPa and 498–570 °C).

Gervilla et al. (2012) suggested that during the retrograde metamorphism, primary chromite of the chromitites from Golyamo Kamenyane reacted with the olivine matrix in the presence of low fO_2 fluids and subsequently with oxidizing Fe^{3+}-rich fluids. This two-stage alteration process produced two distinct features in the chromite grains:

1) Partial to complete replacement of original grains of chromite by a secondary Fe^{2+}-rich porous chromite due to the infiltration of fluids with very low fO_2 at temperatures from ~450 to ~700 °C:
2) Alteration of the chromitites in a late oxidizing hydrothermal event at temperatures below 600 °C, which produced homogeneous (non-porous) ferrian chromite (i.e., Fe^{3+}-rich chromite). This late alteration is confined to localized high-strain zones in the chromitite body.

In this study, we have investigated chromitites classified as zoned and homogeneous (non-porous) chromites according to Gervilla et al. (2012), which were affected by amphibolite-facies tectonometamorphism in the presence of oxidizing Fe^{3+}-rich fluids. These chromites are taken from a late, local high-strain zone (Fig. 1) interpreted to have formed during the retrograde tectonometamorphic event (Colás et al., 2014).

3. Analytical methods

Microstructural analyses including grain size, grain shape and crystallographic relationships and chemical compositions in major elements were conducted by Electron Back-Scattered Diffraction (EBSD), electron microprobe (EMP), and energy dispersive X-ray spectroscopy (EDS), respectively.