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A secondary precious and base metal mineralization in chromitites linked to the development of a Paleozoic accretionary complex in Central Chile

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ABSTRACT

Platinum-group element (PGE) and gold inclusions are usually present in peridotites and chromitite deposits associated with ophiolites. Here, we present the first detailed study of the mineralogy of precious metals in ultramafic rocks hosted in the Paleozoic Coastal Accretionary Complex of Central Chile. In these ultramafic rocks the mineralization of precious metals is associated with small meter-size pods and veins of massive chromitite hosted in serpentinite-filled shear zones. Crystallographic orientation maps of single chromite grains, obtained using the Electron-Backscattered Secondary Diffraction technique, allow us to identify two types of chromite in the precious-metal bearing chromitites: (1) Type A chromite, characterized by an average misorientation per grain of ≤2° and chemically homogeneous cores surrounded by a porous rim with abundant inclusions of chlorite, and (2) Type B chromite, which exhibits higher degrees of misorientation (2–8°) and porosity, and abundant silicate inclusions, but a relatively homogeneous chemical composition. In situ analyses using EMPA and LA-ICP-MS for major, minor and trace elements indicate that composition of the magmatic chromite is only preserved in the cores of Type A chromite grains. Core to rim chemical trends in these Type A chromites are characterized by a progressive increase of the Cr# with a decrease of the Mg#, loss of Al and addition of Fe^{2+} in the porous rim. The observed changes in the microstructure and chemistry of chromite are associated with the infiltration of external fluids through shear zones filled with antigorite (±talc) developed in partly serpentinized peridotites (i.e., olivine–lizardite dunites). Thermodynamic calculations using the phase equilibria relations in the system Cr_2O_3–MgO–FeO–Al_2O_3–SiO_2–H_2O (CrMFASH) indicate that Fe^{2+}-rich porous chromite + chlorite replaced the original assemblage chromite + olivine in the chromitite while prograde antigorite was formed. According to our results this transformation occurred at ~510–560 °C when external fluids penetrated the ultramafic/chromitite bodies through shear zones. These temperatures are slightly higher than estimated for the metamorphic peak in the host metapelitic rocks (i.e., ~420 °C at 9.3 kbar), suggesting that a hotter ultramafic body was captured by the metasediments of the accretionary prism during their exhumation through subduction channel. Chlorite geothermometry yielded a wide range of lower temperature from 430 to 188 °C, for chlorite present in the porous chromite rims. These results are in agreement with the retrograde overprint under greenchist-facies metamorphism conditions recorded by metapelitic host rocks and minor volcanogenic massive sulphide deposits in the area (300–400 °C, ~3–4 kbar). We suggest that although initially decoupled, the chromitite-bearing ultramafic rocks and their metasedimentary host undergone a common metamorphic PT pathway of exhumation during the formation and evolution of the subduction-related accretionary complex.

The chromitites contain appreciable amounts of the platinum-group elements (up to 347 ppb total) and gold (up to 24 ppb), present as inclusions of platinum-group minerals (PGM) and alloys as well as native gold. The PGM identified include native osmium, laurite (RuS_2), irarsite (IrAsS), osarsite (OsAsS), omeiite ($OsAs_2$), Pt–Fe alloy (possibly isoferroplatinum) and a suite of inadequately identified phases such as PtSb (possibly stumpflite), PdHg (possibly potarite), RhS, Ir–Ni and Ir–Ni–Ru compounds. Only a few grains of osmium and laurite were identified in unaltered cores of chromite and therefore considered as magmatic in origin formed during the high-T event of chomite crystallisation in the upper mantle. The other PGM were located in the porous chromite

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associated with chlorite or base-metal minerals (BMM) that often fill the pores of this altered chromite or are intergrowth with antigorite in the host serpentinized ultramafic rock. The assemblage of BMM identified in the studied rocks include sulphides [millerite (NiS), polydymite (Ni_3S_4), violarite ($FeNi_2S_4$), galena (PbS), sphalerite (ZnS), chalcocite (CuS)], arsenides [(orcelite ($Ni_{5-x}As_2$) and maucherite ($Ni_{11}As_8$)], the sulpharsenide gersdorffite (NiAsS), and native bismuth. The irregular shape of several PGM grains observed in porous chromite suggest disequilibrium, whereas others exhibit perfectly developed crystal faces with the associated secondary silicate or base-metal mineral suggesting *neoformation* of PGMs in situ from metamorphic fluids. We suggest that the origin of these PGM inclusions is magmatic, but some grains were reworked in situ when metalloid (i.e., As, Sb, Pb, Zn and Hg)-rich fluids released from metasediments penetrated the ultramafic rocks through active shear zones, once the ultramafic bodies became tectonically mixed with the host metasedimentary host rocks. During this event, gold sourced from the (meta)sediments was also precipitated within chromitites and serpentinites.

1. Introduction

The Chilean Coastal Cordillera extends almost continuously between latitude 32°S and 43°S along the Pacific coast of Chile (Fig. 1a). It is interpreted as an accretionary complex developed at the southwestern margin of Gondwana during the Late Paleozoic (Hervé et al., 1976; Hervé, 1977; Godoy, 1979; Hyppolito et al., 2014a,b). This complex comprises two paired units or metamorphic belts known as the Western Series (to the West) and the Eastern Series (to the East), which were affected by metamorphism at high and low P/T ratios, respectively (Aguirre et al., 1972; Hervé et al., 1988; Willner et al., 2005; Richter et al., 2007; Glodny et al., 2008; Hyppolito et al., 2014a). In the 1960s the Canadian company Lockwood conducted an exploratory geophysical survey across the Coastal Cordillera, which identified numerous magnetic anomalies in the southern part of the Western Series. These anomalies were preliminarly interpreted as iron ores and triggered numerous subsequent lithological and structural studies.

In 1970, researchers of the *Instituto de Investigaciones Geológicas* developed an extensive field campaign in order to identify the cause of these aeromagnetic anomalies (Lockwood Survey Co., 1969). They concluded that some of these magnetic anomalies were not produced by iron ores but that they corresponded to bodies of mafic and ultramafic rocks containing appreciable amounts of iron-bearing minerals (Álvarez and Rivera, 1970; Vergara, 1970). A decade later, Alfaro (1980, 1981) identified chromite ores in the ultramafic body of Lavanderos in the La Cabaña area, approximately 60 km from the city of Temuco (Fig. 1a). Although the aforementioned chromite ores were small and rejected as an economic source of chromium, Alfaro (1980, 1981) observations were a landmark for subsequent studies published at the end of the 90s (Barra et al., 1998; Höfer et al., 2001). These more recent studies provided better constraints on the petrography and composition of the chromite ores and their host rocks cropping out in the area of La Cabaña. However, a detailed interpretation regarding the mechanism(s) of crystallisation and the setting of formation of these chromite ores was not aimed in these studies.

Recently, González-Jiménez et al. (2014a) have used the composition of chromite coupled with the bulk-rock platinum-group elements (PGE) and Re–Os isotopes of the chromite ores from La Cabaña to confirm an ophiolitic origin. They also proposed that the chromite ores were formed beneath a spreading center developed above a suprasubduction zone, in which arc-type melts would mingle within dunite conduits representing channels for the extraction of these melts. Meanwhile, Barra et al. (2014) showed that the infiltration of postmagmatic fluids during regional metamorphism promoted the reaction of magmatic chromite with the olivine matrix, producing rims of secondary Fe^{2+}-rich porous chromite in equilibrium with chlorite.

The data provided by González-Jiménez et al. (2014a) indicate that the chromite ores from La Cabaña concentrated mainly Os, Ir and Ru, producing the negative slope that ophiolitic chromitites characteristically show in the chondrite-normalised PGE patterns. These results are consistent with the presence of few grains of Os–Ir-rich alloys and sulpharsenides identified by Galdames et al. (2011). It is accepted that Os–Ir-rich PGMs can be genetically linked with the crystallisation of chromite at relatively high temperature from basaltic melts (Mungall, 2005; Finnigan et al., 2008; González-Jiménez et al., 2009; Uysal et al., 2009; Pagé et al., 2012). However, they can be also formed by the alteration of pre-existing PGMs or by direct re-precipitation of PGE mobilised during the metamorphic alteration of chromite (Proenza et al., 2008; El Ghorfi et al., 2008; Prichard et al., 2008; Tsoupas and Economou-Eliopoulos, 2008; González-Jiménez et al., 2010). The fact that the chromite ores of La Cabaña underwent significant modification during regional metamorphism suggests a feasible scenario for the formation of a secondary precious metal mineralization. However, the knowledge of the PGE + Au mineralization in the La Cabaña chromite ores is still rudimentary because there is no detailed characterization of the genetic and spatial relationships of unaltered vs. altered chromite, and the potential PGE mineral carriers.

In this contribution, we performed an extensive study of the mineralogy of the platinum-group elements and gold, and their accompanying base-metal minerals (BMM, including sulphides, sulpharsenides, arsenides and antimonides) and silicates found as inclusions in the chromite ores. In addition we undertook a detailed study of the microstructure of the precious metal-bearing chromitites as well as original bulk-rock data for the chromite ores (including PGE + Au). These microstructural and geochemical data were coupled with field observations, and integrated within the framework of a new structural map of the ultramafic bodies, aimed at evaluating the role of shear zones (in partly serpentinized peridotites) on chromite alteration.

In addition, crystallographic orientation maps of single chromite grains, obtained using the Electron-Backscattered Secondary Diffraction (EBSD) technique, were collected to constrain the micro-structural relations between deformation and alteration at the scale of small chromite grains. Furthermore, new EMPA and LA-ICPMS analyses carried out on individual grains of chromite and associated silicates were used to fingerprint the metamorphic signal of chromite and to refine our previous estimates of the PT conditions for the PGM (chromite) host alteration. Finally, these results are used to establish the evolutionary stages of precious metal mineralization within the framework of the Accretionary Complex developed in the Coastal Cordillera of Central Chile during the Paleozoic. In a broad sense, our study constraints the interplay between deformation and fluid infiltration in the formation of precious and base metals ores during regional metamorphism of ultramafic rocks.

2. Geological background

2.1. The Coastal Cordillera of south-central Chile

The Coastal Cordillera of south-central Chile (Fig. 1a) comprises two parallel N–S trending metamorphic belts, the so-called Western and the Eastern series, characterized by different metamorphic gradients and rock assemblages. The Eastern Series comprises slightly deformed