Nanoscale partitioning of Ru, Ir, and Pt in base-metal sulfides from the Caridad chromite deposit, Cuba

JOSÉ M. GONZÁLEZ-JIMÉNEZ1,*,†, ARTUR DEDITIUS1, FERNANDO GERVILLA1,3, MARTIN REICH4, ALEXANDRA SUVOROVA5, MALCOLM P. ROBERTS2, JOSEP ROQUÉ6, AND JOAQUÍN A. PROENZA6

1Departamento de Mineralogía y Petrología, Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain
2School of Engineering and Information Technology, Murdoch University, Murdoch, 6150 Western Australia, Australia
3Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC-UGR, Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain
4Department of Geology and Andean Geothermal Center of Excellence (CEGA), FCFM, Universidad de Chile, Plaza Ercilla 803, Santiago, Chile
5Centre for Microscopy, Characterisation and Analysis (CMCA), The University of Western Australia, Perth, 6009 Western Australia, Australia
6Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona (UB), 08028 Barcelona, Spain

ABSTRACT

We report new results of a combined focused ion beam and high-resolution transmission electron microscopy (FIB/HTEM) investigation of platinum-group elements (PGE)-rich base-metal sulfides. The Ni-Fe-Cu base-metal sulfides (BMS) studied are millerite (NiS), pentlandite [(Ni,Fe)S], pyrite (FeS2), and chalcopyrite (CuFeS2). These BMS were found forming composite inclusions (<60 µm across) within larger unaltered chromite from the Caridad chromite deposit, which is hosted in the mantle section of the Mayari-Baracoa Ophiolite in eastern Cuba. Electron probe microanalysis of BMS revealed PGE values of up to 1.3 wt%, except for pentlandite grains where PGE concentrations can reach up to 12.8 wt%. Based on the amount of Ru, two types of pentlandite are defined: (1) Ru-rich pentlandite with up to 8.7 wt% of Ru and <3.5 wt% of Os, and (2) Ru-poor pentlandite with Ru <0.4 wt% and Os <0.2 wt%. Ru-rich pentlandite contains Ir-Pt nanoparticles, whereas the other sulfides do not host nanometer-sized platinum-group minerals (PGM). The Ir-Pt inclusions are found as: (1) idiomorphic, needle-shape (acicular) nanoparticles up to 500 nm occurring along the grain boundaries between Ru-rich pentlandite and millerite, and (2) nanospherical inclusions (<250 nm) dispersed through the matrix of Ru-rich pentlandite. HRTEM observations and analysis of the selected-area electron diffraction patterns revealed that nanoparticles of Ir-Pt form domains within Ru-rich pentlandite. Fast Fourier transform analyses of the HTEM images showed epitaxy between Ir-Pt domain and PGE-poor millerite, which argues for oriented growth of the latter phase. These observations point to sub-solidus exsolution of the Ir-Pt alloy, although the presence of nanospherical Ir-Pt inclusions in some other grains suggest the possibility that Ir-Pt nanoparticles formed in the silicate melt before sulfide liquid immiscibility. These Ir-Pt nanocrystals were later collected by the sulfide melt, preceding the formation of Ru-rich pentlandite. Early crystallization of the Ru-rich pentlandite and Ir-Pt nanoparticles led to the efficient scavenging of PGE from the melt, leaving a PGE-poor sulfide residue composed of millerite, pyrite, chalcopyrite, and a second generation of PGE-poor pentlandite.

Keywords: Nanoparticles, platinum-group elements (PGE), focused-ion beam (FIB), transmission electron microscopy (TEM), chromite, Cuba; Applications of Fluid, Mineral, and Melt Inclusions

INTRODUCTION

The potential role of nanometer-sized phases during the selective partitioning of platinum-group elements (PGE: Os, Ir, Ru, Rh, Pt, and Pd) has been little explored, particularly under the high temperatures that are typical for magmatic processes. Previous experimental studies carried out in binary mixtures of pure metals indicate that Ir and Pt can form alloys with a face-centered cubic (fcc) structure over a range of temperatures ranging from 975 to 1370 °C (Turchi et al. 2006 and references therein). This is consistent with the fact that Pt-bearing Ir alloys phases have been indeed documented in natural samples.

For example, Pt-bearing Ir alloys (with trace amounts of Os) have been found associated with laurite (RuS3) or pentlandite [(Ni,Fe)S] in mantle peridotites (e.g., Lherz massif in France and Horoman Complex in Japan; Kogiso et al. 2011; Lorand et al. 2010), chromite ores from the Oman ophiolite (Ahmed and Arai 2003) and in magmatic platinum-group mineral nuggets found in rivers draining ultramafic- mafic complexes of the Goodnews Bay in Alaska (e.g., Tolstykh et al. 2002). Additionally, nanometer-sized particles of Ir-bearing Pt alloys have been observed within pentlandite grains in chromite ores from the Bushveld Complex in South Africa (Wirth et al. 2013).

Experimental studies by Peregoedova et al. (2004) show that monosulfide solid solution (mss) with variable amounts of Pt, Ir, and Pd can exsolve discrete Ir-Pt alloys particles during desulfurization (i.e., decrease of sulfur fugacity, °fS2) at magmatic