

# A preliminary study of magmatic and hydrothermal Ni-Cu-Fe-Co sulfides in basic rocks of the external zone of the Betic Cordillera

José María González-Jiménez (1\*), Idael F. Blanco-Quintero (2), Lola Yesares (3), Rubén Piña (3), Amira Rosa Ferreira (1), Igor González-Pérez (4), Erwin Schettino (1,4), Claudio Marchesi (1,4), Lorena Ortega (3), Fernando Gervilla (1,4)

(1) Instituto Andaluz de Ciencias de la Tierra. CSIC-Universidad de Granada, 18100, Armilla (España)

(2) Departamento de Ciencias de la Tierra y del Medio Ambiente, Facultad de Ciencias. Universidad de Alicante, 03690, San Vicente del Raspeig (España)

(3) Departamento de Mineralogía y Petrología, Facultad de Ciencias Geológicas. Universidad Complutense de Madrid, 28040, Madrid (España)

(4) Departamento de Mineralogía y Petrología, Facultad de Ciencias. Universidad de Granada, 18002, Granada (España)

\* corresponding author: [jm.gonzalez.j@csic.es](mailto:jm.gonzalez.j@csic.es)

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## INTRODUCTION

More than 2,000 outcrops of igneous mafic rocks with ages spanning from Triassic to Cretaceous are widespread in the internal and external zones of the Betic Cordillera. This magmatism originated by continental rifting associated to the break-up of the Pangea continent in the Late Permian-Triassic, and subsequent aperture of the Atlantic Ocean from the Jurassic to the Cretaceous (Morata et al., 1997). It comprises submarine basaltic flows plus small subvolcanic dolerite bodies, whose compositions changed from picritic-tholeiitic at the beginning of the Upper Triassic to transitional and alkaline sodic throughout the Jurassic, continuing intermittently until the Upper Cretaceous (Morata et al., 1997). These mafic rocks had significant economic value as industrial material for infrastructure construction and building decoration. More recently, they have been of great interest as resource for the critical raw material graphite from a world's unique sulfur-graphite mineralization near the locality of Huelma in the Jaén province (Luque del Villar et al., 2009). Other styles of mineralization associated to this mafic magmatism include skarn-related Fe-ores from the localities of Garciez in the Jaén province, and Baena in the Córdoba province (Fenoll & García-Rosell, 1975), and those from the Coto Minero de Cehegín in the Murcia province (García-Cervigón et al., 1976). The latter ores from Murcia were exploited until 1989 for Fe and are currently under evaluation by the company Solid Mines España to resume Fe mining. Despite these efforts, to date, there are no comprehensive studies regarding the metallogenic potential for economic metals such as Ni, Cu and Co, which are known to selective concentrate in these types of parental basaltic magmas. In particular, the mineralogy of these metals is still unknown.

## RESULTS AND DISCUSSION

In this preliminary study, we have analyzed whole-rock samples from more than 25 intrusive basic bodies widespread from western (Cádiz) to central (Jaén) and eastern (Alicante and Murcia) portions of the external Betic Cordillera. The results reveal uneconomic concentrations of less than 200 ppm of Ni, Cu and Co, in most of the targeted bodies. Some of the studied bodies, however, contain disseminations (up to 10 % vol) of Fe-Ni-Cu sulfides with Co amounts of less than 1 wt.%. The Fe-Ni-Cu sulfides identified comprise pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ), pyrite ( $\text{FeS}_2$ ), marcasite ( $\text{FeS}_2$ ), pentlandite  $(\text{Ni,Fe})_9\text{S}_8$  and chalcopyrite ( $\text{CuFeS}_2$ ), and they form distinctively different assemblages.

One group of sulfides forms composite aggregates up to 5 mm across, typically exhibiting lobule- and bleb-like morphologies intimately intergrown with primary silicates of the gabbroic rock (pyroxene, plagioclase and olivine). Within these sulfide aggregates, larger pyrrhotite grains host both granular and flame-like pentlandite, which often is bounded by ribbons of chalcopyrite. These minerals and their textures are the typical products of solidification of droplets of Fe-Ni-Cu sulfide melts segregated by immiscibility from the primitive basaltic melt. At  $\sim 1000^\circ\text{C}$ , a

reasonable temperature for the complete solidification of the intruding gabbroic rocks in a thinned crust, a monosulfide solid solution (i.e., MSS;  $Fe_{1-xS}$  to  $Ni_{1-xS}$ ) is expected to be the first solid that crystallized from the sulfide melt containing Fe, Ni, Cu and lesser amounts of Co. According to the condensed phase diagrams in the quaternary Fe-Ni-Cu-S system, at this temperature the MSS can coexist with a sulfide melt enriched in Cu and Ni (Craig and Kullerud, 1969; Ebel and Naldrett, 1996). Upon cooling, the metal excess in MSS is exsolved as pentlandite, first as ribbons at the margin of pyrrhotite ( $\leq 300$  °C), and later as exsolution-like flames at  $\sim 100$  °C (Kelly and Vaughan, 1983). In the Cu-Fe-S portion of the system, however, cooling of the high-temperature precursor intermediate solid solution (ISS) may result in the formation of chalcopyrite. The fact that we identified chalcopyrite forming ribbons around flame-like pentlandite suggests that sub-solidus re-equilibration of ISS into its low temperature product chalcopyrite very likely continued down to lower temperatures ( $\leq 100$ °C; Craig and Kullerud, 1969; Ebel & Naldrett, 1996).

On the other hand, a second group of sulfides includes isolated grains of pyrite, marcasite and/or chalcopyrite (hosting inclusions of sphalerite and galena) with irregular morphologies and grain sizes  $< 1$  mm. This type of sulfides is exclusively associated to infilling veins crosscutting partially altered silicates, being mutually intergrown with, or hosting secondary silicates (i.e., mainly epidote and to a lesser extent sericite and albite), Fe-Mg-rich carbonates and/or oxides (i.e., specular hematite). Here, the formation of sulfides is interpreted to be related with the circulation of hydrothermal fluids that leached Ca and Mg as well as metals (Fe, Ni, Cu and Co) from the basic rock while precipitating the sulfides. The origin of these hydrothermal sulfides is linked to the circulation of relatively hot fluids  $< 250$ °C that promoted the transformation of magmatic plagioclase and pyroxene to epidote and amphibole, respectively, during the prehnite-pumpellyite/lower greenschist facies metamorphism of dolerite.

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