

# The Aguablanca Cu-Ni(PGE) intraplutonic ore deposit (Extremadura, Spain). Isotope (Sr, Nd, S) constraints on the source and evolution of magmas and sulfides

La mineralización intraplutónica de Cu-Ni(PGE) de Aguablanca (Extremadura). Aportaciones de la geoquímica isotópica (Sr, Nd y S) con respecto a la fuente y evolución de los magmas y sulfuros.

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## Abstract

The Aguablanca Cu-Ni(PGE) ore is a case of an intraplutonic ore deposit. It is hosted by mafic and ultramafic cumulates of the Aguablanca Stock, which is part of the larger calc-alkaline Santa Olalla Plutonic Complex of  $359 \pm 18$  Ma age (Rb-Sr whole rock determination). Primary mineralization consists of pyrrhotite, pentlandite and chalcopyrite and resulted from the crystallization of an immiscible sulfide-rich liquid. Several stages of hydrothermal alteration are superimposed. Isotope work on the host igneous rocks (Sr, Nd) and the ore (S), suggests that contamination with a crustal source took place at some depth before final emplacement of the plutons ( $\epsilon Nd_{360} = -5.8$  to  $-7.2$ ;  $Sr_{(360)} = 0.7082$  to  $0.7103$ ;  $\delta^{34}S_{(sulfides)}$  near  $+7.4\%$ ). Assimilation - fractional crystallization (AFC) processes are invoked to explain the chemical variability of magmas.

## Resumen

El yacimiento de Cu-Ni(PGE) de Aguablanca constituye un caso de mineralización intraplutónica alojada en los acumulados máficos y ultramáficos del Plutón de Aguablanca. Este plutón pertenece al Complejo Plutónico de Santa Olalla de Cala, cuya edad, establecida por el método Rb-Sr en roca total, es de  $359 \pm 18$  Ma. La mineralización primaria consiste en pirrotina, pentlandita y calcopirita y se formó por cristalización de un líquido sulfurado, inmiscible con el magma silicatado. Además, se han reconocido varias etapas de alteración hidrotermal superpuestas. La composición isotópica de las rocas ígneas (Sr, Nd) y de la mineralización (S), sugiere que tuvo lugar contaminación con corteza continental a cierta profundidad, previa al emplazamiento definitivo de los plutones ( $\epsilon Nd_{360} = -5.8$  to  $-7.2$ ;  $Sr_{(360)} = 0.7082$  a  $0.7103$ ;  $\delta^{34}S_{(sulfuros)}$  aprox.  $+7.4\%$ ). La diversificación química de los magmas se explica por una combinación de procesos de asimilación y cristalización fraccionada (AFC).

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## Introduction

The Aguablanca Cu-Ni(PGE) ore is a massive intraplutonic sulfide deposit hosted by mafic cumulates of the Aguablanca stock. It is located in SW Spain in Extremadura, very close to the boundary with the Sevilla and Huelva provinces (Fig.1). The deposit is not exposed on the surface and was discovered after a regional geochemical prospection survey carried out by Presur, a Spanish public company, and subsequently drilled and evaluated by Atlantic Copper Holding S.A., venture-

joined with the former. The deposit is pipe-like and subvertical, extending downward for more than 500m, with a thickness of 60 to 100m (Lunar *et al.*, 1997), and is found at few tens of meters from the northern contact of the stock. Host rocks here are marbles and calc silicate rocks replaced by a massive Ca-skarn formed mainly by garnet, clinopyroxene and scapolite (Casquet, 1980).

This is the first ore deposit of this type to be found in Spain. Although it is a small deposit, the similarities with other world class Ni-Cu(PGM) deposits such as

Noril'sk, Råna and Monchegorsk, and the favorable potentiality offered by neighbouring areas make this deposit an interesting target for research.

## Geological setting

The Santa Olalla Plutonic Complex (SOPC) was emplaced in the southern limb of the large Monesterio Antiform, into low-grade metavolcanics and meta-sedimentary rocks of Upper Precambrian-Lower Cambrian age. To the south it ends abruptly against the Zufre Fault (Fig.1). The Monesterio Antiform is part

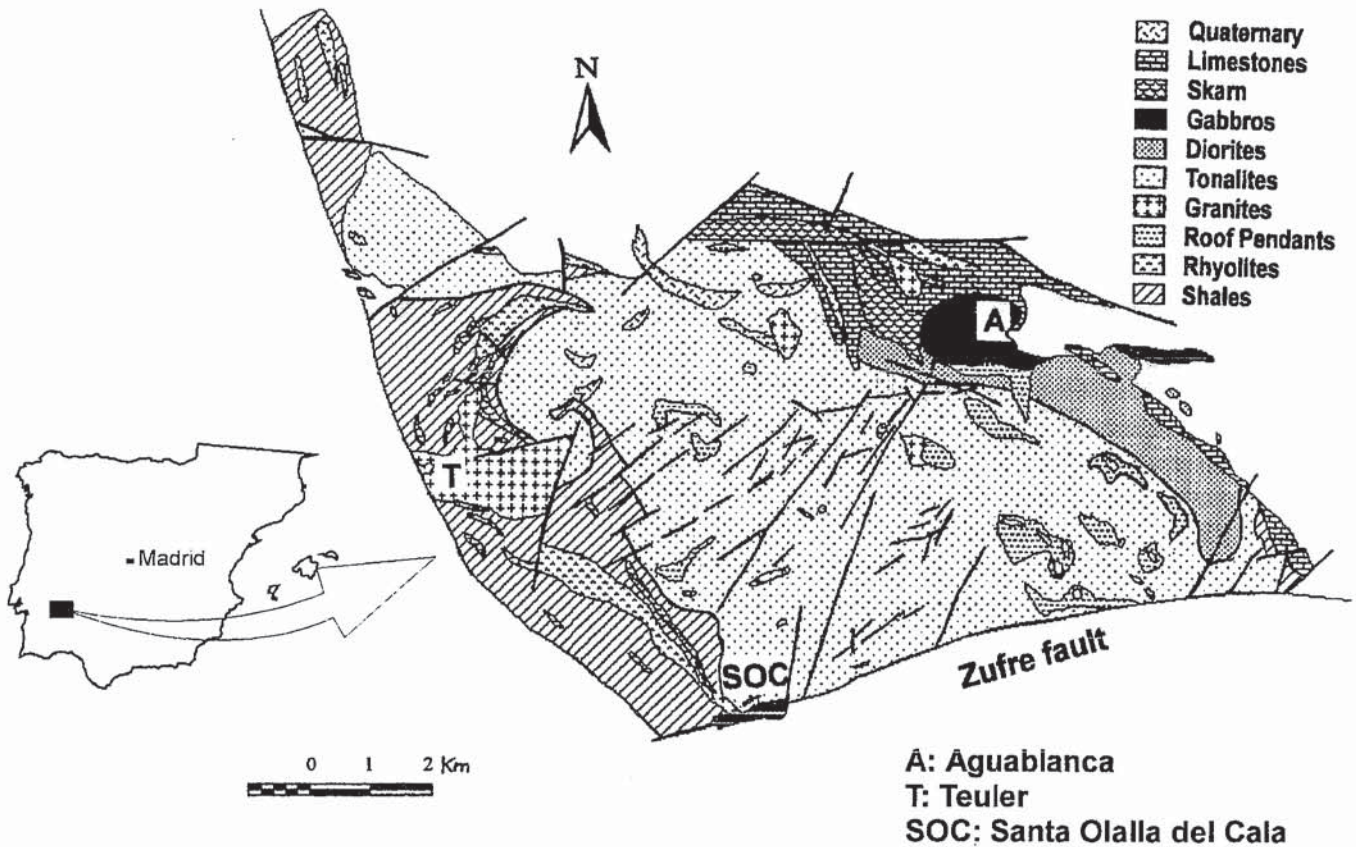


Fig.1. Sketchy geological map of the Santa Olalla Plutonic Complex. Esquema geológico del Complejo Plutónico de Santa Olalla.

of the Ossa-Morena Zone, which is one of the subdivisions of the Hesperian Massif as recognized by Lotze (1945). Regional schistosity and bedding wraps around the pluton. However, in detail, discordances are common, suggesting that an earlier stage of forceful intrusion and/or ballooning was followed by stoping. The latter is indicated by the abundance of roof pendants in the central part of the massif. An aureole of contact metamorphism is well developed around the SOPC with temperature reaching Hypersthene Hornfels facies conditions.

**The igneous rocks**

The SOPC consists of two main epizonal zoned plutons, the Main Santa Olalla Pluton and the Aguablanca Stock (AS), as well as many felsic dykes and small satellite granitic bodies. Emplacement took place at depth of 2-4km (0.5-1kb) according to Casquet (1980, 1982).

The Main Santa Olalla Pluton is the largest intrusion. Compositional zoning of the pluton is pronounced with amphibole-biotite quartz diorites merging into tonalites and these in turn

into granodiorite-monzogranites towards the pluton center (Velasco, 1976, Casquet, 1980). Transitions are gradational. The AS is a small body in the northern part of the SOPC, in contact with the regional host rocks. It is also zoned with cumulates, largely norites, gabbro-norites and websterites, that grade into amphibole-biotite diorites in the core. Sulfide mineralization is hosted by the cumulates.

Chemically two main groups of rocks can be distinguished in the SOPC: 1) the AS cumulates and 2) the Main Igneous Sequence (MIS), formed by the rest of the AS and the Main Santa Olalla Pluton rocks. The first, show SiO<sub>2</sub> contents of 48-57% and are low in K<sub>2</sub>O (<0.7%) reflecting small amounts of biotite. High contents of Ni (300-450ppm) and Cr (740-1200ppm) have been found in the AS cumulates. The MIS consists of metaluminous Hy+Q normative rocks with SiO<sub>2</sub> contents of 55-69% (excluding the small granitic intrusions) and K<sub>2</sub>O values of up to 5%. Ranges of Rb and Sr contents in the Main Igneous Sequence are 45-135ppm and 225-360ppm respectively. The MIS is a case of a calcalkaline K<sub>2</sub>O-rich association (Casquet, 1980).

**The ore**

The mineralization consists mainly of pyrrhotite, pentlandite and chalcopyrite. Textural evidence suggests that several stages of mineral formation were involved in the formation of this ore deposit. The first, probably the consequence of crystallization of an immiscible sulfide-rich liquid, gave rise to massive coarse grained (0.2-3mm) pyrrhotite with fine (50-100 μm) flame-like exsolutions of pentlandite (Ni<sub>0.31</sub>Fe<sub>0.27</sub>S<sub>0.45</sub>) and chalcopyrite intergrowths. Sulfides are interstitial to cumulus silicates. This stage is roughly synchronous or slightly younger, than the crystallization of silicates (pyroxenes and plagioclase mainly) and magnetite. A second stage is evidenced by a new generation of coarse grained recrystallized pyrrhotite (without pentlandite exsolutions), chalcopyrite and pentlandite (NiO<sub>0.24</sub>Fe<sub>0.25</sub>S<sub>0.51</sub>) that replace the earlier sulfides. Minor amounts of mackinawite, rutile and cobaltite were also formed at this stage. A third stage is represented by the transformation of pentlandite to violarite along grain boundaries and fractures, and

the growth of pyrite and new chalcopyrite and pyrrhotite. Finally marcasite formed as late replacements of pyrite and pyrrhotite.

Postmagmatic sulfides might be related to relatively low-temperature alteration processes as suggested by the complementary replacement of igneous minerals by biotite, actinolite, epidote and sericite, among others. The relationships between endo and exo-contact (skarns) alterations are not precisely known as yet.

Lunar *et al.*, (1997) have described PGE minerals such as sperrylite or michenerite associated to pyrrhotite. However the precise significance of these PGM is still unknown.

### Isotope work

Sixteen igneous rocks were chosen for Rb-Sr and Sm-Nd isotope determinations. Rb-Sr results are portrayed in the form of an isochron diagram in Fig. 2. The Nd-isotope composition expressed as  $\epsilon_{\text{Nd}_{360}}$  values (MIS rocks only), range from -5.8 to -7.2. The analytical methods and the data-reduction issues involved are described in Galindo *et al.* (1994). Moreover, twenty five sulfur isotope determination were made on sulfides, particularly chalcopyrite, pyrrhotite, pentlandite and pyrite from the Aguablanca ore and the nearby Cala Fe-(Ca) skarn. The isotope composition of sulfur in ore sulfides is very similar in all samples with a mean close to +7.4‰ ( $\delta^{34}\text{S}_{\text{ep}} = +7.2$  to +7.7‰;  $\delta^{34}\text{S}_{\text{po}} = +7.1$  to 7.8‰;  $\delta^{34}\text{S}_{\text{pent}} = +7.4$ ‰).

### Discussion

#### Origin and evolution of the SOPC magmas

Fig. 2, shows an  $^{87}\text{Sr}/^{86}\text{Sr} - ^{87}\text{Rb}/^{86}\text{Sr}$  isochron plot of MIS rocks. An isochron of  $359 \pm 18 \text{ Ma}$  with a MSWD (Mean Standard Weighed Deviation) of 17.1 can be fitted to these rocks. The resulting initial Sr-isotope composition is 0.7092. The Sr-isotope composition of the SOPC igneous rocks at a reference age of 360 Ma ranges from 0.7082 to 0.7103. Aguablanca cumulates show a very small range of  $\text{Sr}_{(360)}$  values (0.7082-0.7084) whilst most the Main Igneous Sequence rocks show values between 0.7090 and 0.7094. The large MSWD of the MIS isochron plot suggests that causes other than analytical error must be involved in the dispersion of isotopic compositions, either primary compositional heterogeneities or secondary subsolidus alteration. Low-T alteration, although usually weak is

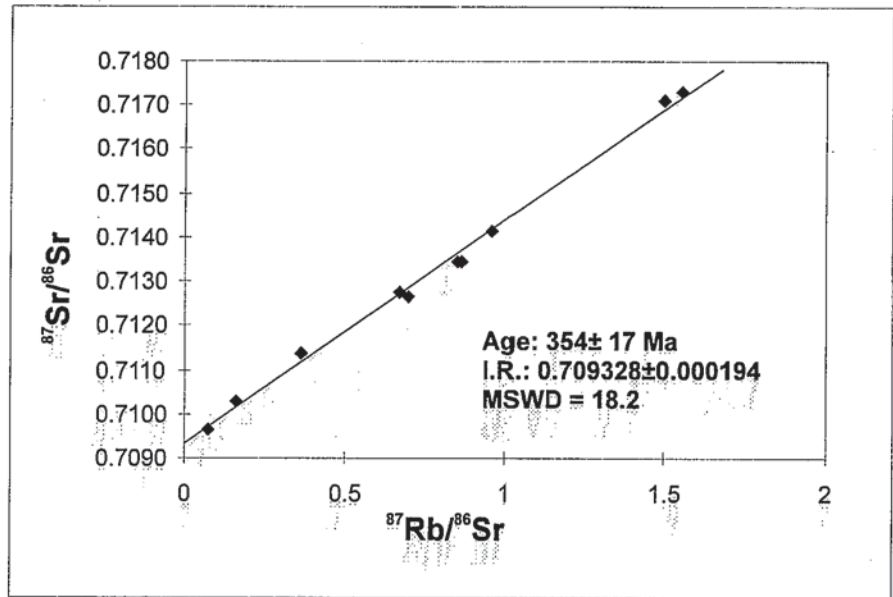


Fig. 2. Isochron diagram of the Main Igneous Sequence rocks of the Santa Olalla Plutonic Complex. Diagrama isócrona de las Rocas Ígneas de la Secuencia Principal del Complejo Plutónico de Santa Olalla.

always present in these rocks. Model ages ( $T_{\text{DM}(360)}$ ) calculated after the method of Borg *et al.* (1990) range from 1.57 to 1.67 Ga.

The Sr and Nd isotope evidence suggests that a source rich in radiogenic Sr and poor in Light REE elements, relative to a depleted mantle, was probably involved in the composition of the SOPC magmas. Moreover Nd-model ages suggest that this component was a continental crust containing old resident Nd. The existence of a circa 2 Ga basement in the Ossa Morena zone has been convincingly argued by Nagler (1990).

Strontium and Nd-isotope composition of the magmas can be modelled in terms of assimilation-fractional crystallization (AFC) processes (De Paolo, 1981). Early crystallization of orthopyroxene in a deep magma chamber accompanied by assimilation of crustal material could lead to an evolution of  $\text{Sr}_{\text{initial}}$  compositions from those shown by the cumulates to those of the MIS magmas. Moreover, the fairly uniform Sr-isotope composition of most of the MIS magmas can be explained by further fractional crystallization of plagioclase at lower pressure accompanied by minor assimilation of crustal material (De Paolo, 1981), probably at or near the final emplacement level. Likewise the Nd-isotope composition of MIS magmas,

which also is very uniform, was probably controlled by amphibole fractionation. Plagioclase and amphibole have high crystal-melt partition coefficients for Sr and Nd respectively. This interpretation contradicts the magma mixing hypothesis proposed by Bateman *et al.* (1992) for the MIS rocks.

The fact that supracrustal biotite-rich metamorphic xenoliths are the only foreign material recognized in these rocks suggests that AFC processes took place in the upper crust, probably at its base. Why magmas with  $\text{Sr}_{\text{initial}}$  signatures lower than 0.708 have not been found probably is the consequence of earlier cumulates, richer in olivine, having been left behind during magma displacement from the deep magma chamber to the final emplacement level.

#### Constraints on the source and evolution of the ore

The S-isotope composition values of the ore sulfides are larger than those typical of juvenile sulfur ( $0 \pm 3$ ‰; Ohmoto, 1986). However they are close - within the error limits - to the upper end of  $\delta^{34}\text{S}$  values of igneous rocks with a strong crustal component (-1 to +7‰; Sasaki and Ishihara, 1979; Matthai *et al.*, 1995). It is interesting to remark here that sulfide mineralizations hosted by Upper Precambrian to Lower Paleozoic slates in the Iberian Massif -probably derived

from remobilization of sedimentary sulfur- show  $\delta^{34}\text{S}$  values between +7 and +21‰. At Mina Sultana, a Cu-Au vein hosted by MSOP tonalites near the western contact of the SOPC, vein sulfides have  $\delta^{34}\text{S}$  values of +10.4 to +14.4‰ (Tornos and Velasco, 1997). In consequence, we think that sulfur in the Aguablanca ore evidences a mixing between a juvenile igneous component and a crustal sulfur in a proportion close to 1:1 (sulfurization; Cheney & Lange, 1967). This conclusion is reinforced by few preliminary  $^{207}\text{Pb}/^{206}\text{Pb}$  values obtained in this ore ( $\mu=9.6-9.8$ ) (Tornos and Chiaridia, unpub.data). The origin of crustal sulfur, whether derived from reduction of sulfates or biogenic is still uncertain.

The solubility of sulfur in basic magmas is very small (Ohmoto, 1986). Exsolution of the S-rich liquid from the contaminated magma probably took place as a consequence of either decreasing temperature, increasing silica activity during differentiation, increasing oxygen fugacity or by a combination of them (Carmichael *et al.*, 1974), during ascent from the deep magma chamber to the final emplacement level of the pluton (2-4km).

#### Constraints on the age of the SOPC

The errochron age of  $359\pm 18\text{Ma}$  referred to above must be taken with caution because of the large age error, and the fact that mixing with a crustal contaminant could provoke a departure from the horizontal of the  $^{87}\text{Sr}/^{86}\text{Sr} - ^{87}\text{Rb}/^{86}\text{Sr}$  line at time  $t=0$ . To check for the latter an independent age determination has been attempted using the K-Ar method on whole rocks. Four determinations have given the following values: 307, 325, 348 and 373 Ma, which are cooling ages. The last two

values are well within the error limits of the errochron age. In consequence we think that  $359\pm 18\text{Ma}$ , i.e., Middle Devonian to Early Carboniferous, is a reasonable estimate of the emplacement age of the MSOP. Younger K-Ar ages are probably representative of the late low-T alteration event shown by these rocks.

The age of the early regional low-grade metamorphism has been estimated by Galindo *et al.* (1988) at  $385\pm 11\text{Ma}$ . Moreover Schafer (1990) quotes a zircon age of 379Ma from a Pulo de Lobo domain granite and relates it with the amalgamation of the Ossa Morena Zone to the South Portuguese Zone, in the course of the Acado-Hercynian Orogeny (Quesada, 1989). In consequence the intrusion of the SOPC probably took place late in this geodynamic scenario.

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