Copper Inclusions in Chlorite from the Aguablanca Ni-Cu-PGE Sulfide Deposit (SW Spain)

/ SAIOA SUÁREZ (1, 2 *), FERNANDO NIETO (2), FRANCISCO VELASCO (1)

(1) Departamento de Mineralogía y Petrología. Universidad del País Vasco, 48940 Lejona (Vizcaya)
(2) Instituto Andaluz de Ciencias de la Tierra y Departamento de Mineralogía y Petrología, Universidad de Granada. 18002, Granada.

INTRODUCTION.

The characterization of base metal-containing sheet silicates has been of long interest in ore deposits aiming to evaluate their potential uses and to understand the geological and physico-chemical processes that allow this metal sorption.

Anomalous copper retention in sheet silicates may represents a useful exploration tool for porphyry copper deposits and has been extensively studied in biotite, chlorite and illite in many deposits worldwide such as those from North America or The Solomon Islands (e.g. Banks, 1974; Rehrig & McKinney, 1976; Ilton & Veblen, 1988, 1992; Ahn et al., 1997). Perhaps the main controversial issues regarding this Cu retention have been the source of Cu and the mode and timing of the Cu-enrichment.

These topics are also evaluated in the present work, which is focused in the outstanding copper retention detected particularly in chlorite and other related sheet silicates from the Aguablanca Ni-Cu-PGE sulfide deposit (Badajoz, Ossa Morena Zone) (Suárez et al., 2006). This study is framed in a well-known metallogenetic context and is developed through the use of specific techniques such as the high resolution transmission electron microscope (HRTEM) is.

MATERIALS AND METHODS.

Sampling was performed on eight weathered sections, from the lower unaltered gabbroic rocks that host the Ni-Cu ore to the upper and more altered horizons below the gossan outcrops of the deposit. Weathering profiles were sampled not only in areas with diseminated sulfides but also in the surrounding barren areas.

An X-ray diffraction study of the samples was carried out using a Philips PW 1710 powder diffractometer with Cu-Kα radiation. Electron microprobe analyses (EMPA) were performed on a Cameca-MBX and Jeol JMS6400 EMP (accelerating voltage of 15kV, beam current of 10nA and beam diameter of 1-2μm) (Basque Country University). Four representative samples were prepared in thin sections with Canada balsam, ion-thinned using a Gatan 600 ion mill and carbon coated for a HRTEM study (CIC, Granada University).

COPPER-BEARING CHLORITE.

Chlorite occurs as an ubiquitous hydrothermal phase within most part of the weathering profiles and represents the best example of Cu-containing sheet silicate in Aguablanca.

Bulk EMP analyses revealed that chlorite belongs to the clinochlore variety. However, Cu-rich chlorite ($\leq 12.5\%CuO$) is limited to the weathered parts of mineralized profiles whereas chlorite in the fresh host rock or within barren profiles has no Cu in the composition (< 0.11 and < 0.13 %CuO, respectively).

Cu- chlorite occurs as detrital fragments within horizons and also fills fissures cross-cutting the profiles, where it achieves the highest Cu content. Average structural formula obtained from these highly Cu-enriched chlorite crystals (28^+charges, Fe as Fe^{2+}, n=13 analyses) is:
$(K_{0.01-0.02}$ $Na_{0-0.01}$ $Ca_{0.02-0.04})_{0.04-0.06}$ $(Mg_{3.04-3.25}$ $Al^{VI}_{1.14-1.33}$ $Cu_{0.34-0.72}$ $Fe^{2+}_{0.37-0.67}$ $Ni_{0.27-0.37}$ $Mn_{0.02-0.03}$ $Ti_{0.02-0.03})_{5.61-5.79}$ $(Si_{3.08-3.31}$ $Al^{IV}_{0.69-0.92})_{4.0}$ O_{10} $(OH)_8$

The XRD study (Suárez et al., 2006) indicated a gradual alteration of chlorite towards the upper and more weathered horizons of the profiles. During supergene alteration, chlorite is being partially altered to smectite and minor vermiculite. In addition, chlorite is progressively transformed from the *IIb* to *Ia* structures defined by Bailey (1988) for the chlorite polytypism.

New conducted HRTEM observations in this chlorite have revealed large areas of well defined 14.0-14.2Å packets, though areas with saponite intergrowth are common. Thus, irregular alternations of chlorite and thin 10-10.2Å packets of smectite are commonly developed. Low-charge corrensite (24.0-24.2Å) may also occur reflecting some interestratification between both phases. Chlorite in highly disrupted areas is partly vermiculized increasing basal spacings up to 14.5-15.0Å. But the most outstanding feature observed in this chlorite is the occurrence of hundreds of small Cu-particles along the crystals (Fig 1).

Analytical electron microscope (AEM) analyses carried out in the least Cu-contaminated layers of chlorite (n=12), provide the following average structural formula (28^+ charges, Fe as Fe^{2+}):
$(K_{0-0.12}$ $Ca_{0-0.17})_{0-0.21}$ $(Mg_{2.41-3.82}$ $Fe^{2+}_{0.38-1.80}$ $Al^{VI}_{0.83-1.39}$ $Cu_{0-0.59}$ $Ni_{0.07-0.48}$ $Mn_{0-0.09}$ $Ti_{0-0.07})_{5.61-6.02}$ $(Si_{3.01-3.45}$ $Al^{IV}_{0.55-0.99})_{4.0}$ O_{10} $(OH)_8$

These analyses show a clear inverse tendency between Mg and Cu (r=-0.75) whereas Mg/Fe correlation is poorer (r= -0.57). Tetrahedral substitution is variable but Si average content is rather high (3.27afu). Some interlayer cations are detected and the total octahedral cations average value is of 5.71afu, which is low to some extent.

It is noteworthy that Cu average content recorded using AEM (0.16afu) decreases significantly compared to the bulk Cu content obtained using EMPA (0.55afu). These last higher Cu contents must be the result of Cu-particles dispersed within chlorite layers.

COPPER INCLUSIONS.

Copper was found widespread in chlorite as submicrometer inclusions (from 5 to 150nm wide and up to 1500nm large) (Fig 1A). These are mainly located within the alteration domains of chlorite, along or close to, interlayers that are slightly expanded.
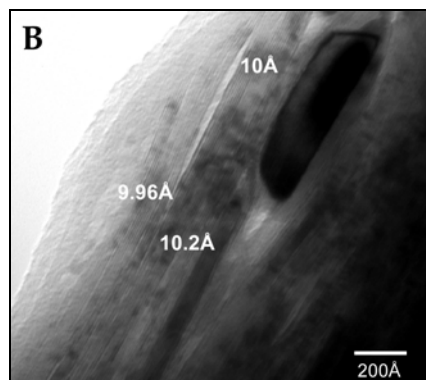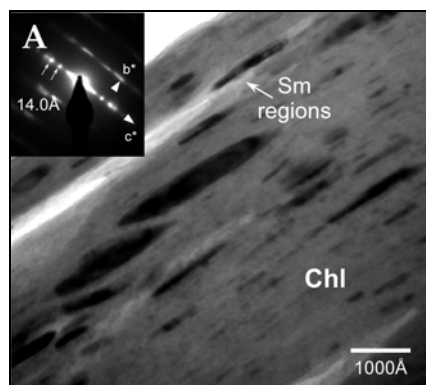

fig 1. TEM images of chlorite crystals containing Cu inclusions (black particles). A) Textural TEM image parallel to c*. SAED pattern of chlorite layers is inset. B) HRTEM image parallel to c* with smectite around a polygonal Cu particle. Chl chlorite; Sm smectite.

Copper nanoparticles enclosed in layers of chlorite (14Å) are scarce, rounded or elongate, and smaller than those inclusions located within the interlayer regions (Fig 1B). In these last areas Cu inclusions are flattered and occasionally show a polygonal morphology. They often appear as single inclusions although sporadically are overlaped in the same region. Within these alteration domains smectite is often developed showing basal spacings of 10Å to 12Å.

EDX analyses carried out in large Cu particles showed that no other element apart from Cu form these inclusions, and therefore a native structural state is deduced. Cu-inclusions were observed also in smectite and occasionally in phlogopite within weathered horizons.

DISCUSSION.

Ilton & Veblen (1988) demonstrated that Cu can occur mainly as inclusions of pure native Cu in the interlayer regions of sheet silicates, which can indeed act as a Cu sink and not as source for primary mineralization as was previously thought. Although Cu inclusions of hydrothermal origin are common, Ilton & Veblen (1992) proved that these particles might be also produced during supergene processes.

This seems to be as well the case in Aguablanca. Both newly formed secondary sheet silicates and some of those inherited from hydrothermalism and partially transformed during weathering, show anomalous Cu content in their composition. Chlorite, as the main Cu-bearing sheet silicate in Aguablanca, is altered to some extent and do not conform exactly to an ideal chlorite composition. Some smectite-vermiculite contamination cannot be ruled out considering the obtained formulae, with both high Si and interlayer cations such as Ca. However, this seems to be a typical feature of metastable sheet silicates which retain base metals as the supergene alteration in ore deposits proceeds.

Copper in Aguablanca occurs mainly as native particles but it is also structurally bounded to sheet silicates as was confirmed by AEM analyses. The supergene source of this Cu is inferred from: (a) the heterogeneous distribution of Cu particles along the crystals but showing a recurrent location within altered interlayer regions, (b) the highly variable Cu content that occurs structurally bounded to these phases, (c) the restricted location of the Cu-bearing sheet silicates, which are only present within the weathered horizons of mineralized profiles, and (d) the special position of these horizons within iluviation areas, optimal to receive potential leached elements from above areas as the gossan zone.

Oxidation of Ni-Cu-PGE sulfide ores at Aguablanca has formed gossaneous rocks in shallow areas of the orebodies. The strong oxidizing and acidic to neutral conditions achieved in these upper levels have almost certainly encouraged the leaching of the most mobile metals like Cu. Perhaps a great part of this Cu is captured by goethite or other Fe-rich stable minerals within the gossan zone. However, that Cu leached could have been partly retained within

the lower, iluviation zones of the profiles given the suitable weathering conditions and favoured by the presence of base metal scavengers such sheet silicates can be.

Within these weathered horizons over the gabbro, neutral to basic pH conditions dominate (pH~6-8). However, the lack of oxidation turns this deeper parts of the profiles into a more reducing environment compared to the superficial gossan zone. This situation would be highly favourable for the development of native Cu particles that are conveniently allocated in sheet silicates.

This study shows the importance of the local supergene conditions in the process of heavy metal retention, and how the use of high resolution techniques becomes essential for the accurate identification of base metal-bearing phases.

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