Serpentine As a Natural Nickel Scavenger in Weathering Profiles of the Aguablanca Ni-Cu-(PGE) Deposit (Spain). A SEM and HRTEM Study

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Desintegration of Ni-Cu-(Platinum group elements) sulphides during supergene alteration in the Aguablanca deposit (Badajoz, SW Spain) has resulted in the partial release of base-metals at low temperature conditions. Specially Ni and Cu are being variably retained by several inherited and neoformed mineral phases throughout the developed weathering profiles. A detailed study of these phases using electron microscopy has allow to describe and analyze accurately a neoformed serpentine that represents the main Ni-bearing silicate within the profiles. This serpentine resembles Ni-lizardite and reaches contents of up to 42%wt. NiO. The different mechanisms for metal retention in serpentine are also discussed since nickel occurs both structurally bounded and sorpted as pure native particles. This study examines the processes that contribute to the natural retention of metals in sheet silicates during the exogenic cycle.

INTRODUCTION

Fine-grained minerals developed during supergene alteration of silicates in base-metal sulphide deposits might play a significant role in controlling the heavy metal fate originated from the oxidation of sulphides during the exogenic cycle. Iron and manganese oxides or hydroxides, preferably developed in the upper parts of the weathering profiles, are known scavengers of heavy metals in ore deposits (e.g. Thornbern, 1979). Nevertheless, sheet silicates concentrated in the lower parts of the profiles could also play a potentially important influence on metal retention in mining areas due to their well-known sorption capacity.

Minerals of the serpentine group are common examples of highly Ni-enriched phases during weathering processes and have been reported in worldwide mineral deposits (e.g. lateritic nickel deposits from Brazil, New Caledonia, Australia, etc.). The Ni analogues of lizardite and chrysotile (nepouite and pecoraite, respectively) can retain much more than a 30% of NiO, becoming frequently one of the main Ni-bearing phases in alteration zones of mineral deposits. Especially interesting are those nepouites in intimate mixture with kerolites (10 Å talc) or other hydrous silicates that may form the distinctive garnierite in the supergene domain. However, the common fine-grained and inhomogeneous character of those minerals made their study very difficult and few detailed compositional analyses in natural samples have been published.

This study examines the formation of a Ni-rich serpentine in the weathering profile of the Aguablanca Ni-Cu-(PGE) magmatic sulphide deposit (Ossa Morena Zone, SW Spain) (e.g. Tornos et al., 2006 and references therein). The use of high-resolution techniques has allowed a detailed analysis of almost monomineralic areas of Ni-serpentine and the evaluation of the different sorption mechanisms of Ni related to the present weathering conditions at low temperature.

MATERIALS AND METHODS

Four representative samples from the Aguablanca weathering profiles were selected for this study. They were collected in the southern orebody of the deposit, above the unaltered host gabbronorite intrusive of the Aguablanca Stock. X-ray diffraction studies of both the < 2 mm and the < 2 μm fractions were carried out using a Philips PW 1710 Powder Diffractometer with Cu-Kα radiation, (University of the Basque Country). The carbon coated samples (< 2 mm) were examined by a LEO 1430-VPSEM instrument with a 3.5 nm spatial resolution and operating at an accelerating voltage of 20 kV, using BSE imaging and EDX analysis, (CIC, Granada University).

Due to the very fine grained nature of the serpentine crystals, two samples were selected for a detailed HRTEM study. The thin sections were prepared with Canada balsam, ion-thinned using a Gatan 600 ion mill and carbon coated. HRTEM lattice-fringe images and electron diffraction patterns from selected areas (SAED) were obtained in a Philips CM20 (STEM) with a LaB6 filament, equipped with an EDAX solid state EDX detector operating at 200 kV, (CIC, Granada University).

WEATHERING PROFILES. OCCURRENCE OF SERPENTINE

Supergene alteration in the Aguablanca deposit has formed immature, 6-8 meter-thick weathering profiles above the unaltered host gabbro and below the gossan (10m thick), where base-metal sulphide oxidation took place. These profiles typically show several horizons related to the main physical and chemical properties of the underl-

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ying host rocks and variable degrees of supergene metal enrichment. Thus, a ~40 cm thick clay-rich horizon (with contents up to 56% of phyllosilicates) was developed overlying the unweathered gabbro. Compared to other horizons within the profile, this clay-horizon shows a clear Ni-Cu enrichment (contents up to 6000 ppm and 3900 ppm, respectively) even though the lack of sulphides (< 0.3% S). Chemical properties are characterized by a neutral pH [6.7 - 7.0], with a moderate humidity percentage (35%) and a cation interchange capacity up to 56.28 cmolq/K.

The mineralogical and geochemical study of these horizons showed that commonly neoformed secondary phases such as smectites, vermiculites or Fe-oxides and oxyhydroxides are here acting as Ni-Cu-carrying phases. Values of up to 3.8% NiO and 4.0% CuO were measured for those phases. However, neither the common inherited primary silicates nor their hydrothermal alteration products contain significant Ni or Cu in their mineral composition. Commonly, this mineral mixture is dominated by amphiboles, pyroxenes, chlorite, talc, phlogopite and plagioclases. Most of these mineral phases show NiO and CuO contents of up to 0.31% and 0.17%, respectively.

The only exception is the well preserved hydrothermal chlorite, which displays the maximum contents of Ni and Cu detected in both neoformed or inherited silicates within the profile (values of 12.5% NiO and 9.06% CuO). A supergene retention of Ni is deduced since chlorite from the lower fresh host rocks does not display significant Ni contents (maximum values of 0.76% NiO). This trioctahedral Ni-clinochlore occurs widespread throughout the weathering profile as detrital fragments dispersed in the horizons (300 µm in size) and to a lesser extent as centimetric crystals filling thin veins that cross cut the profiles (Suárez et al., 2005).

A detailed high-magnification study of this chlorite has revealed the formation of serpentine minerals intergrown within the chlorite, reaching contents of up to 42% in NiO. This serpentine is not related to the serpentinisation process underwent by the deposit which is restricted to the ultramafic enclaves within the Aguablanca Stock. The following section describes the main characteristics of the identified serpentine.

CHARACTERIZATION OF THE SERPENTINE

Serpentine occurs at the submicroscopic scale penetrating into chlorite layering and growing at the expense of it *(Fig. 1A)*. It is mainly located at the edges of chlorite crystals, filling spaces between layers, along cracks or as a coating in cavity walls or another textural defects along the layers. In detail, serpentine displays a microcrystalline character forming aggregates often crumbled and mixed with small fragments of chlorite. Low magnification TEM images normally show vuggy edges of chlorite filled with disordered arrangements of serpentine layers folded at the edges.

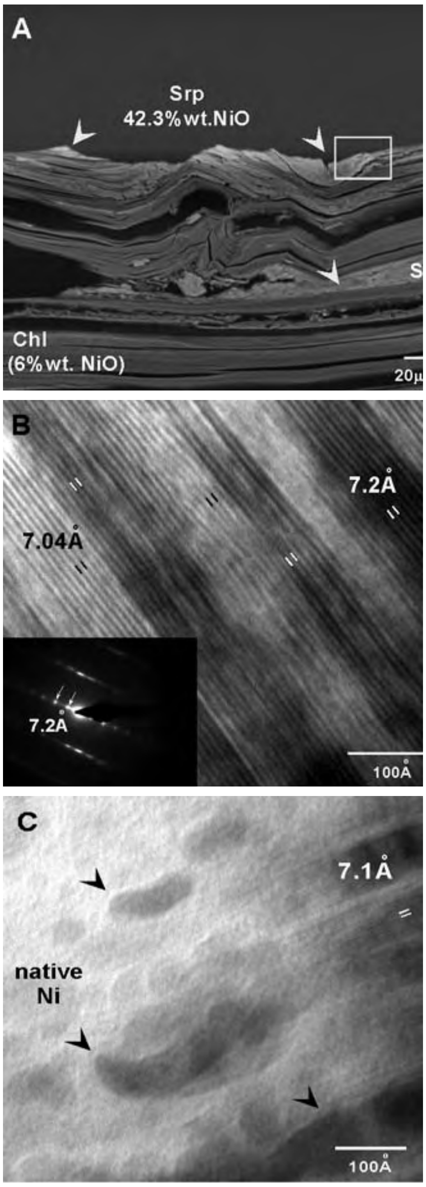

Fig. 1. A) BSE image of an ion-thinned chlorite sample. B) Lattice fringe image of a monomineralic Ni-serpentine and its corresponding SAED (inset). C) Pure native Ni particles in the surface of serpentine layers.

High resolution images of those regions (Fig. 1B) reveal large areas in which well-defined 7.1-7.3 Å packets are developed. Boundaries between chlorite and serpentine are characterized in most of the cases by regular alternations of thin 14 Å packets and well developed 7 Å packets, suggesting some intergrowth between both phases at this scale. Serpentine seems to crystallize mainly in monomineralic stacks although occasionally, SAED patterns in more disrupted areas have shown some smectite contamination. This is a very common feature of Ni-enriched serpentines, but well defined fringes with spacings of 10 Å were not detected in the lattice-fringe images.

AEM analyses of the serpentine (n=12) were carried out in apparently uncontaminated areas showing regular stackings of the layers. The following average structural formula was obtained calculated on the basis of a total cation valence of 28 positive charges and assuming all the Fe as Fe^{+2}:

$$(Ca_{0.02\text{-}0.19}, K_{0\text{-}0.05})_{0.02\text{-}0.24}$$
$$(Mg_{1.22\text{-}2.36}\ Al^{VI}_{0.18\text{-}1.16}\ Fe^{+2}_{0.20\text{-}1.37}$$
$$Ni^{+2}_{1.58\text{-}3.49}\ Cu^{+2}_{0\text{-}0.19}\ Ti^{+4}_{0\text{-}0.17}$$
$$Mn^{+2}_{0\text{-}0.02})_{5.51\text{-}6.02}\ (Si^{+4}_{2.96\text{-}4.06}$$
$$Al^{IV}_{0\text{-}1.04})_{4\text{-}4.06}\ O_{10}\ (OH)_{8}$$

This serpentine is characterized by high Ni contents of up to 3.49 afu, with an average value of 2.65 afu and high standard deviation of 0.66. In many cases, nickel occurs as the dominant divalent octahedral cation, with lower Mg, Fe and Al contents. Cu, Mn and Ti contents are low whereas Co and Cr were not detected. The total octahedral cations range from 5.51 to 6.02 with an average value of 5.72 and a low standard deviation of 0.18. Nickel and magnesium show a clear inverse tendency (r = -0.811, Pearson correlation coefficient) probably being isomorphously replacing each other in different proportions. Besides, Ni shows a good negative correlation with Al^{VI} (r = -0.713) but is poorly correlated with other chemical parameters. Tetrahedral substitution is variable; some analyses showed a substantial excess of silica and were rejected. Total Al and Si are moderately correlated (r = -0.621).

This studied serpentine is classified as an intermediate phase between the Mg and Ni end-members and should be considered as the nickeloan form of the magnesian mineral (Ni-lizardite) when Mg > Ni and Ni is ≤ 3.0 afu $R_6Si_4O_{10}(OH)_8$ (≤ 30% wt. NiO). Other crystals fall closer to Ni end-members of the isomorphous series when Ni > Mg and Ni > 3 afu. In such cases, the serpentine shows here Ni contents between 3.13 and 3.49 afu, and they can be considered as nepouites (Brindley, 1978). The chemical composition of this serpentine falls into the "garnierites field" delimited by Gleeson et al. (2003), ranging from kerolite to pimelite (Mg, Ni-talc minerals) and from serpentine to Ni-bearing serpentine (nepouite).

Here, serpentine seems to occur preferably as a nickel lizardite-nepouite rather than as another polymorphic form of the serpentine mineral group. Particularly useful in their identification are the morphological characteristics and the XRD patterns since nepouites and pecoraites have the same chemical formula. In this case, serpentine occurs in aggregates displaying a platy morphology with a flat layering, which is in strong contrast to the typical fibrous nature and cylindrical layering of the chrysotile-pecoraite species.

XRD data are less conclusive since an effective separation of the serpentine and the host chlorite was not achieved. The basal spacing of the serpentine is close to half that of chlorite and the reflections coincide almost exactly with all even-order chlorite peaks. This situation produces a rational 00l diffraction pattern fixed, in which rational positions are unaffected by the common treatments. On the basis of the weak reflections, the presence of the 1.50 Å peak might indicate the occurrence of nepouite since pecoraite only displays a strong reflection at ~1.53 Å. Regarding to the layer stacking sequence, the strong 2.387 Å reflection or the invariable absence of the 2.49 Å peak are probably indicative of the group A (2M1>1M=3T) defined by Bailey (1969) for the polytypism of trioctahedral 1:1 layer silicates. The most intense reflection at 2.326 Å of the group B and the 1.945 Å peak of the group B and D are also absent on the XRD patterns. According to Bailey (1969), group A is characteristic of a relative low structural stability.

Nickel was also found occasionally as anhedral particles of pure native Ni on the surface of the analyzed specimens (*Fig. 1C*), particularly in highly altered areas. These particles have a globular-elongated shape viewed parallel to the serpentine sheets, and small sizes between 3 and 30 nm. Areas of 100-150 nm display a high density of superimposed particles following almost the same direction of the sheets. EDX analyses suggest that no other elements apart from Ni are present. Therefore, a native structural state can be deduced.

DISCUSSION AND CONCLUSIONS

Serpentine occurs as an accessory mineral in the middle-low parts of weathering profiles but represents the main Ni-bearing silicate in the supergene domain of the Aguablanca deposit. Chemical and textural studies of the nickeliferous serpentine have revealed two different mechanisms for the Ni retention during the exogenic cycle:

(i) Ni metal structurally bounded

Serpentine shows different Ni contents between the Mg and Ni end-members as the result of a variable degree of replacement of Mg^{+2} by Ni^{+2}, presumably due to their similar ionic size and equal charge. In general, these intermediate minerals do not conform exactly to the theoretical formula of a normal serpentine structure, and it is quite difficult to supply completely satisfactory formulae. In this case, some analyzed areas showed some silica excess and deficiency of R^{+2} ions. Some authors (e.g. Brindley, 1978) suggested that this deficiency is possibly caused by leaching at the edges of the clay particles. The leaching not only would remove soluble R^{+2} ions and OH^- from the edge positions, but also could leave a residue of silica. Nevertheless, impurities from silica-rich phyllosilicates in some areas cannot be totally excluded. Smectite formation in some areas could explain the silica enrichment or the minor quantities of Ca^{+2} or K^+ occasionally recorded.

(ii) Ni metal as pure native particles

These nanoparticles do not share the typical properties shown by metallic nickel particles commonly found in high temperature environments (e.g. Nickel, 1959). Besides, Ni enrichment is here restricted to the oxidized rocks within the weathering profiles, so their origin is more congruent with the supergene domain. Nickel-rich products associated with sheet silicates during weathering are hardly documented. Their physical and chemical properties make difficult an accurate classification with the usual techniques, so nickel oxides and hydroxides are commonly deduced due to the oxygen detection during the analytical procedures. In Aguablanca, part of the nickel seems to occur as a pure native metal suggesting that the local weathering conditions might have been critical. Further observations are required to determine the precise environmental and geochemical conditions of this process.

The characteristics of the Ni-serpentine developed at Aguablanca evidence the variability of the substitution of Mg by transition metals during the weathering, with heterogeneous distribution of the Ni along the hydrous silicate layers. These common heterogeneities are thought to be related to the different local growth conditions of the minerals with possible influence of disequilibrium conditions, and moreover, to the different weathering conditions at low temperatures, which certainly play an important role in the processes of Ni supergene enrichment (Manceau and Calas, 1985).

The correct determination of the sorption mechanism of metals on clays and other mineral surfaces must be an important target for understanding the fate of such pollutants and could facilitate successful environmental remediation procedures. This research adds to the understanding of the processes that affect the natural retention of metals in the subaereal environment.

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