macla nº 20. julio 2015
revista de la sociedad española de mineralogía



# Ni-Enrichment Processes Revealed by TEM Imaging on Garnierites

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## INTRODUCTION

Ni-phyllosilicates, commonly grouped under the name of "garnierites", are significant nickel ores found in hydrous silicate-type Ni-laterite deposits worldwide. They usually occur as vein infillings in the lower parts of laterite profiles, and consist of fine-grained, often intimately mixed, nickel-magnesium phyllosilicates, including serpentine, talc, sepiolite, smectite and chlorite (e.g. Brindley & Maksimović, 1974).

In the Falcondo Ni-laterite deposit (Dominican Republic), garnierites are composed of: i) mixtures between serpentine and hydrated talc-like phases (kerolite-pimelite), and ii) sepiolite-falcondoite, according to previous XRD, optical microscopy, SEM and EMPA (e.g. Villanova-de-Benavent et al., 2014). These results show that garnierite mixtures with large amounts of talc-like (kerolite-pimelite) have in general higher Ni contents than serpentine-dominant garnierites. This is coherent with earlier studies reporting that Ni concentrated mainly in the talc-like phases (Soler et al., 2008; Galí et al., 2012).

They often occur as poorly crystalline, micron-scale mixtures, so data obtained by conventional methods may not be conclusive. Transmission Electron Microscopy (TEM) is revealed as a useful technique to unravel the relationships among the mineral assemblages at the nano scale in garnierites. However, very few detailed TEM works on Ni-bearing Mg-phyllosilicates exist up to the present (e.g. Uyeda et al., 1973; Pelletier, 1983; Suárez et al., 2011), and high resolution imaging and electron diffraction studies are in general scarce. Furthermore, most of these publications are based on crushed and dispersed material onto TEM grids, and therefore the textural information of the assemblages is lost.
This study presents further information of the features involving serpentine and talc-like particles in garnierite mixtures from samples preserving the original textures. The aim of this work is to shed some light in the formation of garnierites, and to unravel the Ni-enrichment processes occurring in the Ni-laterite profile.

## MATERIALS AND METHODS

Two samples were examined under TEM for this study, corresponding to the types I and II described and analysed in detail in Villanova-de-Benavent et al. (2014). The samples, labelled 09GAR-2 and LC-100AB, consist of serpentine- dominant garnierite mixtures with talc-like (kerolite-pimelite) particles.

The samples were prepared as polished thin sections with a thermo-fusible resin. Representative areas containing garnierites to be studied by TEM were selected under the optical microscope. A copper grid including the area of interest was glued on the thin section, cut and subsequently detached. Finally, the grids were ion milled, using a Gatan 600 Duo Mill, and carbon coated. The instrument used was a Jeol JEM 2010 operating at 200 kV, equipped with an EDX spectrometer, from the Università degli Studi di Siena.

## RESULTS AND DISCUSSION

Serpentine-dominant garnierite mixtures are formed by cylindrical and/or polygonal serpentines, with well defined ~7 Å spacings, in a matrix of talc-like (kerolite-pimelite) particles, displaying characteristic ~10 Å lattice fringes.

The sample LC100AB is composed by 15-sectored, well-developed polygonal serpentines with diameters around 6000 Å and tiny hollow cores, and other cylindrical serpentines with sizes over 2000 Å, large cores and incipient sectoring, surrounded by kerolite-pimelite (Fig. 1a). Looking in further detail into the serpentines, kerolite-pimelite fibres fill the large cores and are observed to emerge from the outer borders of the cylinders (Fig. 1b). The sample 09GAR-2 consists of large polygonal serpentines (up to 20.000 Å in diameter), coexisting with smaller cylindrical serpentines (between 500 and 2000 Å in diameter) in a matrix of kerolite-pimelite thin, short fibres (Fig. 1c).

These textural features observed under TEM altogether may suggest that talc-like fibres form after the serpentine particles, taking advantage of borders (outer rims, inner walls of cores), and discontinuities (contact between sectors). It is worth noting that there is a characteristic porosity inside the sectors of the polygonal serpentine, possibly linked to the formation of kerolite-pimelite wavy fibres from serpentine (Fig. 1c-d).

In general, serpentine-dominant garnierite mixtures, with talc fractions between 0.14 and 0.31 (calculated according to Brindley & Hang, 1973), have systematically low Ni contents (below 1.0 apfu Ni) when compared to garnierites with remarkable amounts of kerolite-pimelite (0.89–3.44 apfu Ni, calculated on the basis of 11 oxygens), as indicated by EMPA point analyses (Villanova-de-Benavent et al., 2014). Furthermore, the individual serpentine particles analysed by TEM-AEM yield up to 0.6 apfu Ni, whereas Ni in kerolite-pimelite fibres coexisting with them range from 0.7 to 2.1 apfu.

On one hand, these TEM-AEM results are coherent with the previous information obtained by means of XRD and EMPA, which indicated that Ni is predominantly concentrated in the talc-like phases instead of in the serpentine particles. Actually, the Ni-dominant serpentine (népouite or pecoraite) has not been reported in the Falcondo Ni-laterite, but the occurrence of népouite has been

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| ***palabras clave:*** Garnierita, Filosilicatos de Níquel, Serpentina Poligonal, Kerolita-Pimelita, MET, República Dominicana. | ***key words:*** Garnierite, Ni-Phyllosilicates, Polygonal Serpentine, Kerolite-Pimelite, TEM, Dominican Republic. |



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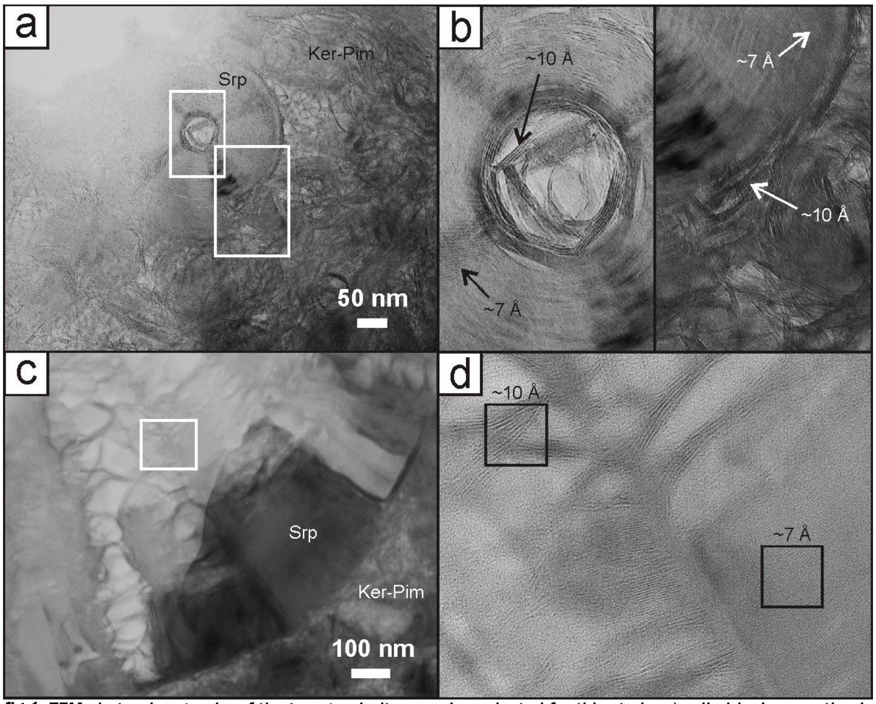


*fig 1. TEM photomicrographs of the two garnierite samples selected for this study: a) cylindrical serpentine in a talc-like matrix in specimen LC-100AB; b) high resolution images of the areas included in white rectangles in "a)"; c) polygonal serpentine surrounded by talc-like fibres in specimen 09GAR-2; d) detailed view of the area in the white rectangle in "c)". Legend: Srp (serpentine), Ker-Pim (kerolite-pimelite).*

extensively documented in some deposits of New Caledonia (e.g. Brindley & Wan, 1975). The difference between Falcondo and New Caledonian Ni-laterites may be explained by the lithology of the primary ultramafic rocks. In New Caledonia, the protolith is mainly harzburgite and dunite (e.g. Pelletier, 1983), whereas in the Dominican Republic it is mostly clinopyroxene-rich harzburgite and lherzolite (e.g. Marchesi et al., 2012). The higher content in pyroxene may indicate higher activity of silica in the Dominican than in the New Caledonian Ni-laterites, leading to the preferential formation of talc-like phases rather than serpentine during weathering.

On the other hand, the later formation of kerolite-pimelite from serpentine particles is in accordance to the garnierite precipitation model proposed by Galí et al. (2012). This model is based on that in an Al-free system such as the Falcondo laterite profile, the stability of serpentine, kerolite–pimelite or sepiolite–falcondoite is mainly controlled by the silica activity. As a result, the ideal formation of the Ni ore occurs as a successive precipitation of mineral phases progressively enriched in Ni and Si, because silica activity increases with time and through the profile. Thus, the first garnierite-forming phase to precipitate is serpentine (lizardite–népouite), followed by kerolite–pimelite, sepiolite–falcondoite and Ni-free sepiolite with quartz (Galí et al., 2012).

## *FINAL REMARKS*

In conclusion, the results obtained on garnierites from the Falcondo Ni-laterite presented in this contribution indicate that Ni-enriched kerolite-pimelite fibres replace Ni-poor serpentine particles. These observations are coherent with previous mineralogical, textural, geochemical and thermodynamical studies, and may explain the process of progressive Ni-enrichment within garnierites.

## *ACKNOWLEDGEMENTS*

This research has been financially supported by the Spanish projects CGL2009-10924 and CGL2012-36263, a FPU-PhD grant and a "Estancias breves" scholarship to CVdB from the Ministerio de Educación (Spain). The help and hospitality extended by the staff at Falcondo Xtrata mine are sincerely acknowledged. The authors are also grateful to the sample preparation personnel at the Universidad de Granada and the Università degli Studi di Siena.

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