Ni-phylllosilicates (garnierites) from the Falcondo Ni-laterite deposit (Dominican Republic): Mineralogy, nanotextures, and formation mechanisms by HRTEM and AEM

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Abstract

Ni-bearing magnesium phyllosilicates (garnierites) are significant Ni ores in Ni-laterites worldwide. The present paper reports a detailed TEM investigation of garnierites from the Falcondo Ni-laterite deposit (Dominican Republic). Different types of garnierites have been recognized, usually consisting of mixtures between serpentine and talc-like phases that display a wide range of textures at the nanometer scale. In particular, chrysotile tubes, polygonal serpentine, and lizardite lamellae are intergrown with less crystalline, talc-like lamellae. Samples consisting uniquely of talc-like and of sepiolite-falcondoite were also observed, occurring as distinctive thin lamellae and long ribbon-shaped fibers, respectively. HRTEM imaging indicates that serpentine is replaced by the talc-like phase, whereas TEM-AEM data show preferential concentration of Ni in the talc-like phase. We suggest, therefore, that the crystallization of Ni-bearing phyllosilicates is associated with an increase in the silica activity of the system, promoting the replacement of the Ni-poor serpentine by the Ni-enriched talc-like phase. These results have interesting implications in material science, as garnierites are natural analogs of Ni-bearing phyllosilicate-supported synthetic catalysts. Finally, SAED and HRTEM suggest that the Ni-bearing talc-like phase corresponds to a variety of talc with extra water, showing larger d001 than talc (i.e., 9.2–9.7 Å), described as “kerolite”-“pimelite” in clay mineral literature.

Keywords: Ni-laterites, garnierites, chrysotile, polygonal serpentine, lizardite, “kerolite”-“pimelite”, sepiolite-falcondoite, HRTEM

Introduction

Garnierite was originally the name of a mineral species discovered in 1863 in New Caledonia (Garnier 1867), although it was later proved to be a mixture of different Ni-hydrous silicates (e.g., Pecora et al. 1949; Faust 1966). Since then, the term garnierite has been widely used in the literature to refer to the group of green, fine-grained, poorly crystallized, Ni-bearing magnesium phyllosilicates, including serpentine, talc, sepiolite, smectite, and chlorite, often occurring as mixtures (e.g., Faust 1966; Brindley and Hang 1973; Springer 1974; Brindley 1978; Wells et al. 2009; Villanova-de-Benavent et al. 2014a). Therefore, despite not being a valid mineral name, garnierite became a convenient field term used by mine geologists to designate all green Ni-phylllosilicates when a more specific characterization was not possible (Brindley 1978), and many authors have used this term with this general meaning (e.g., Moraes 1935; Pecora and Hobbs 1942; Pecora et al. 1949; Varela 1984; Gleeson et al. 2003, 2004; Freyssinet et al. 2005; Wells et al. 2009).

In addition, the classification and naming of the garnierite minerals represents a complex, long-lasting controversy because of their fine-grained nature, poor crystallinity, and frequent occurrence as intimate mixtures of different mineral species (Brindley and Hang 1973). Brindley and co-authors, after various studies, distinguished the following Mg-Ni series: the serpentine group minerals (1) lizardite-népouite and (2) chrysotile-pecoraite; (3) berthierine-brindleyite; the talc-like structures (4) talc-willemsite and (5) “kerolite”-“pimelite”; (6) the chlorite series clinoclore-nimite; and finally (7) sepiolite-falcondoite (Brindley and Hang 1973; Brindley and Maksimović 1974; Brindley 1978, 1980). The most common garnierites found in nature are formed by lizardite-népouite and “kerolite”-“pimelite” (Brindley 1978), and many authors have been referred to them as “serpentine-like” (or “7 Å-type”) and “talc-like” (or “10 Å-type”) garnierites, respectively (e.g., Brindley and Hang 1973; Brindley and Maksimović 1974; Wells et al. 2009; Gali et al. 2012). “Kerolite” and “pimelite” can be described as phases with talc affinity and extra water in their structure, within the ideal structural formula (Mg,Ni),Si₄O₁₀(OH)₂·n(H₂O). Faust (1966) classified “pimelite” into the smectite group, although other authors proved that neither “kerolite” nor “pimelite” exhibit intracrystalline swelling (e.g., Kato 1961; Brindley and Hang 1973; Brindley 1978). Regardless being both discredited species by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC-IMA), these names have been used during the following decades (e.g.,
The remarkable Ni content of garnierites makes them significant Ni ores in some Ni-laterite deposits, such as in the Falcondo deposit, in the Dominican Republic (e.g., Golightly 1981; Elias 2002; Gleeson et al. 2003; Freyssinet et al. 2005). In the Falcondo Ni-laterite, characterized by an Al-poor ultramafic protolith, five garnierite types were distinguished according to their color, mineralogy, textures, and chemical composition (namely types I to V, Villanova-de-Benavent et al. 2014a, 2014b): (I) Ni-Fe-bearing serpentine-like, (II) Ni-bearing mixture of serpentine-like and “kerolite”-“pimelite”, (III) Ni-dominant mixture of serpentine-like and “kerolite”-“pimelite”, (IV) “kerolite”-“pimelite”, and (V) sepiolite-falcondoite.

These previous results, obtained by means of X-ray powder diffraction (XRD), optical and scanning electron microscopy (SEM, with energy-dispersive spectrometry, EDS), and electron microprobe (EMP), indicated that, in general, the garnierites from Falcondo are complex mixtures at the nanometer scale (Villanova-de-Benavent et al. 2014a, 2014b). Although the methods used are sufficient for a description of the phases from an economic point of view, a detailed study including textures at the nanometer scale is necessary, to unravel the characteristics of the various mixtures and to gain further insight into the distribution of Ni.

Transmission electron microscopy (TEM) is a powerful technique to study the mineralogy, chemistry, and textural features of phases that commonly occur as poorly crystalline, fine-grained mixtures at the nanometer scale. It has been extensively used to study phyllosilicates and, in particular, this method allows distinction of the different minerals of the serpentine group (e.g., Baronnet and Devouard 2005; Andréani et al. 2008; Suárez et al. 2011; Mellini 2013).

Serpentine group minerals are 1:1 triocahedral phyllosilicates that develop different structural forms because of a geometrical misfit between tetrahedral and octahedral sheets. The three most common varieties are (1) lizardite planar lamellae, (2) chrysotile tubes, and (3) antigorite modulated structures. In addition, other microstructures may be found, such as polygonal serpentine, which develop sectored rolled fibers, larger than chrysotile tubes, and (3) antigorite modulated structures. In addition, other microstructures may be found, such as polygonal serpentine, which develop sectored rolled fibers, larger than chrysotile tubes, and (3) antigorite modulated structures.

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However, a limited number of exhaustive TEM works on Ni-bearing Mg-phyllosilicates exist up to the present (Uyeda et al. 1973; Esson and Carlos 1978; Poncelet et al. 1979; Pelletier 1983; Soler et al. 2008; Tauler et al. 2009; 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, omitting the textural information of the assemblages and the relationships between different phases.

This paper presents a textural and chemical characterization by TEM of the different garnierites described in the Falcondo Ni-laterite deposit. The aim of this work was to describe the textural relationships between the different garnierite-forming minerals and to determine the distribution of Ni at the nanometer scale based on high-resolution TEM (HRTEM) and analytical electron microscopy (AEM).

**Geological setting and garnierite occurrence**

Hydrous silicate Ni-laterites of the Falcondo deposit are developed on the Loma Caribe, an ophiolitic peridotite belt in the Cordillera Central in the Dominican Republic. This belt consists of an elongated body, 4–5 km wide and 95 km long, oriented NW-SE and bounded by major faults (Figs. 1a and 1b). The Loma Caribe ultramafic rocks, formed in the upper mantle, are composed of harzburgites, dunites, and lherzolites, partially altered to serpentinites during their emplacement to the present day tectonic position (Lewis et al. 2006; Proenza et al. 2007). Partially serpentinitised peridotites have been exposed to weathering and erosion since the early Miocene, when the laterization process began (Lewis et al. 2006).

The Falcondo Ni-laterite profile is up to 60 m thick and is divided into two main zones or horizons: the limonite on the top and the saprolite at the bottom (Fig. 1c; Haldemann et al. 1979; Lithgow 1993; Lewis et al. 2006). However, the contacts between subzones and their thicknesses vary vertically and laterally in all outcrops of the Falcondo deposit (Lewis et al. 2006; Villanova-de-Benavent et al. 2014a; Aiglsperger et al. 2015).

Garnierites in the Falcondo Ni-laterite occur mainly as millimeter-to-centimeter vein infillings in fractures, as thin coatings on joints and along fault planes, and as clasts and/or cements in different kinds of breccias. They are usually found within the lowermost part of the saprolite horizon, but may also be located near the unweathered serpentinitized peridotite rocks, at the base of the lateritic profile, and in the upper saprolite horizon (Tauler et al. 2009; Villanova-de-Benavent et al. 2014a).

**Materials and methods**

Forty samples from the lower saprolite horizon containing different garnierite types were previously identified by X-ray powder diffraction (XRD), observed by optical and scanning electron microscopy (SEM-EDS), and analyzed by electron microprobe (EMP) at the Centres Científics i Tecnologies de l’Universitat de Barcelona (CCT-UB) (Villanova-de-Benavent et al. 2014a). From these 40 samples, 9 were selected as the most representative to be studied by transmission electron microscopy for the present work (Table 1). Three different methods of specimen preparation were combined, due to the difficulties posed by the friability of the material, and 12 grids were prepared with similar outcomes.

First, some samples were prepared as polished thin sections with Canada balsam. Representative areas containing garnierites to be studied by TEM were selected under the optical microscope. Copper grids were attached on the thin sections, and 12 grids were prepared with similar outcomes.

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methods preserve the original texture of the mineral phases. Third, other samples were separated by hand-picking, ground in an agate mortar, suspended with ethanol and put on a copper grid to obtain additional, higher-quality EDX analyses (e.g., Lopez Munguira and Nieto 2000; Abad et al. 2001). Both ion-milled samples and powders were carbon-coated prior to the TEM study.

The TEM study was performed by Philips CM20 (CIC-UGR) and a Jeol JEM2010 (UniSi), equipped with energy-dispersive X-ray spectrometer detectors (EDS-Oxford Isis, respectively) and operating at 200 kV. Additional images and electron diffraction patterns were obtained using a Jeol JEM2100 at 200 kV (CCIT-UB) as well.

Atoms per formula unit (apfu) were calculated from the atomic concentrations obtained by AEM and based on the theoretical number of positive charges of each mineral (14, 22, and 32 for serpentine, talc, and sepiolite, respectively). Fe was calculated as Fe\(^{3+}\), following Villanova-de-Benavent et al. (2014a) and according to the Fe\(^{2+}/Fe^{3+}\) XANES maps obtained in equivalent samples (Roqué-Rosell et al. in review).

**Results**

TEM results are shown in Figures 2 to 7, including a photograph of the selected sample (Figs. 2a–6a), a photomicrograph of the ion thinned specimen (Figs. 2b–6b), and low-magnification, high-resolution images and electron diffraction patterns. A comparison between the chemical compositions of the minerals
obtained with TEM-AEM and EMP is shown in Figure 8, and AEM analyses are presented in Table 2.

**Mineralogy and textures at the nanoscale**

**Ni-bearing serpentine-dominant (type I).** Type I garnierite consists of serpentine particles and minor talc-like bent thin lamellae with very little porosity (Fig. 2c). Serpentine occurs as tubes of various sizes that are randomly oriented, as basal and longitudinal sections are observed in low-magnification images. There are two groups of serpentine tubes: (1) thick, short tubes up to 5000 Å long and about 3000 Å in diameter, with 85 Å in diameter hollow cores; and (2) less abundant, narrow, long tubes up to 3000 Å in length and around 750 Å in diameter, with ~50 Å hollow cores (Fig. 2d). These nanostructures together with the particle size indicate that this sample is formed mostly by polygonal serpentine in relatively short fibers, finely intermixed with talc-like lamellae. Uyeda et al. (1973) also reported short, stubby tubes with central holes in serpentine-like garnierites from Brazil, with an average width of 740 Å (4.4 wt% NiO; serpentine-talc mixture with a talc fraction of 0.13), with less abundant ill-defined platy fragments, which may resemble the talc-like particles in type I garnierite (Figs. 2c and 2d).

As seen in Figure 2d, the short tubes display bending at the fiber tip. These features have also been observed in polygonal serpenites coexisting with polyhedral serpenites by Andréani et al. (2008). In the high-resolution images of the short tubes longitudinal sections 7.3 Å spacings are observed, in some cases presenting dislocations (Fig. 2e). The 7.3 Å spacings were confirmed in both the electron diffraction patterns and the fast Fourier transform obtained for the same short tubes, which displayed few reflections of the h0l plane that can be indexed with the clinochlore-2M₁₄ 14 Å structure (Brindley and Brown 1980) (Fig. 2f). However, no high-resolution images of the long tubes could be obtained due to electron beam damage. According to the total diameters and the measured spacings, the short, thick ones have approximately 200 T-O layers and the long, thin ones have 50 T-O layers.

**Ni-bearing mixture of serpentine- and talc-like particles**

**Type II.** In the specimen of type II garnierite, serpentine particles, with characteristic 7.2 Å spacings, display various shapes and sizes and are found scattered in a matrix of talc-like bundles (Figs. 3c and 3d). Some serpentine basal sections have diameters around 5000 Å with tiny hollow cores, and are divided in 15 equidimensional sectors with an angle of 24° between adjacent (001) lattice planes, so-called polygonal serpentine (Fig. 3e). In some cases, polygonal sections are kidney-shaped, resembling the polyhedral serpentine of Andréani et al. (2008) (Fig. 3f). The inner diameter of some polygonal serpentine is similar to the outer diameter of the chrysotile basal sections in type I (Fig. 3g). Other serpentine particles display less rounded cylindrical fibers, probably corresponding to oblique sections of serpentine tubes, smaller than the polygonal fibers (up to 3000 Å in diameter), which are hollow-cored or contain disordered layers in the center, probably of a talc-like phase (Fig. 3g). Uyeda et al. (1973) also observed those features and mentioned that this material in the cores could be amorphous. Talc-like lamellae were also observed to concentrate in curved aggregates (Fig. 3h).

**Ni-dominant mixture of serpentine- and talc-like particles (type III).** Type III garnierites display long and bent lamellae with basal fringe spacings of 9.2–9.4 and 7.2–7.4 Å mixed in single particles (Figs. 4c–4e), which are frequently parallel to each other (Figs. 4d–4e). Lamellae of 7.2–7.4 Å spacings are curved, more regular and thicker (from six to sixteen 7.2–7.4 Å spacings) when compared to the 9.2–9.4 Å lamellae (four fringes mostly, and up to six) (Figs. 4c–4e). This is supported by electron diffraction patterns, showing that the sample is composed of crystalline lizardite with a 7.2 Å spacing, coexisting with a lower crystallinity talc-like phase (Fig. 4f). No polygonal serpentine was found and only one basal and one longitudinal section of chrysotile tubes were observed in the specimen. Similar features involving ~7 and ~10 Å structures were observed in a garnierite from Oregon (18.6 wt% NiO, X_{Ni} = 27%) by Uyeda et al. (1973). These values differ from those of the type III garnierite (29–50 wt% NiO and average X_{Ni} of 47%), Villanova-de-Benavent et al. (2014a). Garnierites from New Caledonia shown by Pelletier (1983) and references therein also displayed comparable features.

**Talc-like particles (type IV).** The specimen containing Ni-“kerolite”-“pimelite” garnierites is very homogeneous, as it consists uniquely of sets of superimposed and/or platted, thin, apparent lamellae with two to six basal spacings of 9.5–9.7 Å (Figs. 5c, 5d, and 5e), confirmed by the absence of ~7 Å fringes in this specimen. Identical textures were observed in 10 Å-type garnierites from Brazil by Esson and Carlos (1978), in which no other crystalline phases were detected either. These Brazilian garnierites under the optical microscope display botryoidal features and coexist with silica, like type IV garnierites (Villanova-de-Benavent et al. 2014a). The small particle size, together with the wide and diffuse rings observed in the electron diffraction patterns (typical of a random polycrystalline pattern), suggest that the sample may have low crystallinity (Fig. 5f).

**Sepiolite-falcondoite (type V).** The obtained TEM bright field images demonstrate the presence of Ni-rich sepiolite
roughly oriented in fine ribbons with lengths above several hundreds of nanometers (Figs. 6c and 6d) and frequently enclosed within an amorphous silica matrix (Figs. 6b, 6c, and 6e). The high-magnification image in Figure 6e shows a normal section of the fiber with the well defined (110) crystalline planes. This image allows measuring the 12 Å spacing typical of sepiolite-falcondoite (Post et al. 2007; Tauler et al. 2009).

Mineral chemistry at the nanoscale

The composition of garnierite-forming minerals obtained by AEM is represented in Figure 7, compared to previous analyses obtained by EMP (Villanova-de-Benavent et al. 2014a), and in Table 2. The identification of the mineral species based on the lattice fringe spacing and that from the chemical composition were coherent. In addition, to increase the number of analysis of each mineral species, additional analyses were obtained on particles deposited on copper grids (e.g., López Munguira and Nieto 2000; Abad et al. 2001).

In general, Al is virtually absent in the Falcondo garnierites. Serpentinite particles have low Ni, up to 0.2 apfu in type I and 0.6 apfu in type II; and yield remarkable amounts of Fe, 0.1–0.4 apfu in type I and up to 0.3 in type II garnierites. Type III compositions are actually mixed analyses of lizardite lamellae and the talc-like phase, with Ni contents ranging from 2.7 to 3.3 apfu and Al and Fe below detection limits. Talc-like analyses from all the studied garnierite types yield highly variable Ni contents, between 1.2 to 2.3 apfu (1.7 on average), and Al and Fe are generally low (up to 0.13 apfu Al, 0.03 on average; and up to 0.04 apfu Fe, <0.01 on average). In addition, Ni content in talc-like particles increases gradually from type I to type IV garnierites (Fig. 7).

AEM results plot within or near the compositional fields previously obtained through EMP in the same samples (Villanova-de-Benavent et al. 2014a), although type III mixtures and some analyses of type II serpentines still deviate toward the “kerolite”-“pimelite” series. Even if in most cases it was impossible to obtain pure analysis of the constituent phases of the mixture due to the very small size of the individual packets (e.g., Figs. 4c, 4d, and 4e), the AEM spot size of tens of nano-
The EMP spot size of one micrometer gives unique results of the preferential partitioning of Ni in talc-like particles rather than in the associated serpentines. In summary, the higher spatial resolution of AEM analyses allowed better discrimination than EMP analyses, with slight deviations from the average composition obtained by EMP toward the respective constituent.
end-members (Fig. 7).

Finally, the EDS spectra in type V garnierite enabled distinction of the Ni-sepiolite ribbons from the surrounding matrix. The Ni-sepiolite fibers show a distinctive Ni and Mg content in addition to Si and O, and the presence of Si seems to be related not only with sepiolite but also with amorphous $\text{SiO}_2$ matrix. Ni contents varied from 1.2 to 2.2 apfu and Al and Fe were below detection.

**Discussion**

**Nanotextural variability of garnierite from the Falcondo Ni-laterite**

As stated by Brindley (1978), most garnierites are a mixture of serpentine-like and talc-like phases, and previous TEM imaging studies reported the occurrence of some garnierites as intimate mixtures of 7.2–7.4 and 9.2–9.4 Å basal spacings (e.g., Uyeda et al. 1973; Poncelet et al. 1979; Soler et al. 2008). Most garnierites from the Falcondo Ni-laterite deposit (Figs. 2–5) actually consist of mixtures of different relative proportions of serpentine and talc-like phases (“kerolite”-“pimelite”). TEM analysis distinguished a wide variety of textures and mineral species of the serpentine minerals in the different garnierite mixtures (chrysotile tubes in type I, polygonal serpentine in type II, lizardite lamellae in type III). In addition, TEM revealed the presence talc-like particles in all the serpentine-bearing garnierites even when these had not been detected by XRD, as in type I, probably due to their small quantity and low crystallinity.

Another characteristic feature is that 7.2–7.4 Å fringes occurred in large numbers, whereas 9.2–9.7 Å fringes occurred in smaller sets (as stated by Uyeda et al. 1973), suggesting a lower crystallinity of talc-like phases, which is coherent with their broad peaks, or absence of them, in powder X-ray diffraction (Villanova-de-Benavent et al. 2014a) and with the diffuse and weak ring-shaped electron diffraction patterns in this study. Kato (1961) also reported that talc-like garnierites from New Caledonia produced ring-shaped selected-area electron diffraction patterns (SAED) patterns, whereas serpentine-like phases gave single-crystal diffraction patterns with well-defined spots. Furthermore, Pelletier (1983) (and references therein) distinguished the electron diffraction pattern of the talc-willemseite,
with a regular structure, from the “kerolite”-“pimelite”, showing
centric circles. Other studies reported unspecified disordered
regions in the TEM photomicrographs as well (e.g., Uyeda et al.
1973; Brindley 1978; Esson and Carlos 1978).

Such low crystallinity of the talc-like phase could be related
to specific conditions, such as very low temperature, high wa-
ter availability, and/or high growth rate during crystallization.
The fact that the 10 Å fringes are less regularly defined than
the 7 Å ones, could be also explained by a variable degree of
hydration of their interlayers (Brindley and Hang 1973; Uyeda
et al. 1973) and/or possible volatilization phenomena under the
TEM vacuum.

Finally, sepiolite-falcondoite occurs as an independent phase,
never mixed with serpentine nor talc-like garnierites. It displays
the characteristic elongated ribbon shape of sepiolite, commonly
related to amorphous silica and/or quartz, but has a remarkably
higher Ni content (26.8 wt% NiO) when compared to sepiolites
examined under TEM in other localities (maximum 3.3 wt%
NiO in Indonesia; Kuhnel et al. 1978).

Preferential Ni concentration in the talc-like structure

According to AEM, talc-like phases yield higher Ni con-
centrations than serpentine, which is coherent with the good
correlation between Ni content and the talc fraction in the gar-
nierites from Falcondo, as suggested by Gali et al. (2012) and
Villanova-de-Benavent et al. (2014a), and by Soler et al. (2008),
in the Loma de Hierro Ni-laterite (Venezuela). The higher resolu-
tion of the AEM with respect to EMP enabled distinction of the
serpentine particles from the “kerolite”-“pimelite” lamellae (Fig.
7), despite it being difficult to obtain pure, single-phase analyses
of talc-like or serpentine in type III. Therefore, the distribution
of Ni between serpentine and talc-like phases in type III could
not be well established because of its finer particle size.

Despite Uyeda et al. (1973) stating that there was no correla-
tion between Ni content and morphology of the particles under
TEM, and between proportions of platy and elongated particles
and the number of serpentine-like and talc-like layers (equivalent
to serpentine or talc fraction, respectively), other studies reported
that Ni is mostly concentrated in talc-like phases (e.g., Esson
and Carlos 1978; Poncelet et al. 1979). Besides, Vitovskaya
and Berkhin (1968) also showed some low-magnification and
electron diffraction patterns of what they described as Mg- and
Ni-bearing “kerolites” (actually garnierite mixtures). They
identified typical, tiny clinochrysotile tubes in Mg-“kerolite”
(consisting predominantly of serpentine with Ni below detec-
tion limit), and scales with tiny tubes of clinochrysotile in the

Figure 5. Type IV (kerolite-pimelite) as seen under the TEM (specimen LC-100B). (a) Image of the sample, the specimen was detached from the area in the red rectangle. (b) Detail of the hole in the grid under the optical microscope (plane-polarized light). (c) Low-magnification images of the specimen showing bundles of talc-like lamellae. (d) High-resolution images of talc-like lamellae: (e) close-up of image d displaying the typical basal spacings of talc-like minerals and (f) electron diffraction image. All TEM images were obtained in a Philips CM20 (CIC-UGR). (Color online.)
Ni-“kerolite” (mostly a 10 Å mineral with 11.3 wt% NiO). Consequently in this case Ni was also related to a 10 Å phase. Furthermore, Poncelet et al. (1979) showed by EMP analyses and by heating experiments that most of the nickel was concentrated in the octahedral layer of the 10 Å phase, and not homogeneously distributed in the octahedral layer of both the 7 and 10 Å. During these experiments, metallic Ni particles were deposited onto the 10 Å flakes and rarely onto the serpentine fibers after heating the sample. In addition to these observations and interpretations, our AEM data confirm that the Ni was preferably contained in the talc-like phase. Possibly, the TOT talc structure is more likely to host Ni than the TO serpentine structure, as demonstrated by the equilibrium constants of the simultaneous precipitation of Ni-serpentine and “kerolite”-“pimelite” (Galí et al. 2012).

AEM results of garnierites from the Falcondo Ni-laterite showed that Ni concentration in serpentine is lower than in the talc-like particles, and always below 50% of the total elements in octahedral coordination. Therefore, neither népouite nor pecoraite, the Ni analogs of lizardite and chrysotile, respectively, are found in the garnierites from the Falcondo Ni-laterite deposit. However, the presence of népouite and pecoraite is widely reported in other localities. In particular, népouite has been extensively studied in New Caledonia (e.g., Brindley and Wan 1975; Wells et al. 2009 and references therein). One possible explanation for the different mineralogy between New Caledonian and Dominican Ni-laterites is the lithology of the primary ultramafic rocks. In New Caledonia, the protolith is mainly harzburgite and dunite (e.g., Pelletier 1983, 1996), whereas in the Dominican Republic the protolith is mostly clinopyroxene-rich harzburgite and herzolite, commonly intruded by microgabbro and dolerite dykes (e.g., Marchesi et al. 2012). The greater pyroxene content may imply a greater availability of silica in the Falcondo Ni-laterite deposit, leading to the preferential formation of talc rather than serpentine during weathering.

When examined under TEM, népouite usually occurs as highly crystalline plates (34.8 wt% NiO, Montoya and Baur 1963; 47.6 wt% NiO, Manceau and Calas 1985), whereas pecoraite develops coils and spiral shapes with three to five revolutions about the spiral axis (Faust et al. 1969, 1973; Milton et al. 1983). In contrast, the serpentine particles in Falcondo present larger diameters and lengths than the Ni-dominant counterparts described in the literature. Roy and Roy (1954) and Milton et al. (1983) suggested that the substitution of Mg by Ni in chrysotile gives rise to non-tubular but also not well formed, platy crystals. The Ni substitution probably prevents the tubes to grow up to several hundreds of angstroms and to develop well-rounded spirals or

**Figure 6.** Sepiolite-falcondoite (type V) as seen under the TEM (specimen GAR-7v). (a) Image of the sample, the specimen was detached from the area in the red rectangle. (b) Detail of the hole in the grid under the optical microscope (plane-polarized light). (c) Low-magnification image of the specimen showing sepiolite ribbons in a matrix of amorphous silica (obtained in a Jeol 2010, CCIT-UB). (d) Detailed view of criss-cross sepiolite ribbons (in a Philips CM20, CIC-UGR). (e) Detail of 12 Å fringes of a Ni-sepiolite ribbon oriented normal to the beam, in the matrix of amorphous silica (Philips CM20, CIC-UGR). (Color online.)
concentric tubes. Accordingly, despite that the serpentine particles in type III were not analyzed by AEM due to their small particle size, the possibility of these serpentine lamellae yielding higher Ni contents than the chrysotile tubes and polygonal serpentine in types I and II cannot be discarded.

The formation mechanism of garnierites in the Falcondo Ni-laterite

Low-magnification and high-resolution images are fundamental to understand the genetic relationships between serpentine (in most cases, polygonal fibers) and Ni-rich, talc-like phases. The talc-like lamellae are observed inside the serpentine central hole (Figs. 8a, 8b, and 8e), surrounding the serpentines, forming at the very edges of the particles (Figs. 8a, 8c, 8d, and 8f) and at the boundaries between adjacent sectors of the largest polygonal serpentines (Figs. 8e and 8f). In addition, HRTEM details indicate that, at the reaction front, the (001) talc-like planes are parallel to the 001 serpentine ones. This textural evidence suggests that talc-like phases form after serpentine, taking advantage of high stress sites, such as the outer rims (where the basal planes of serpentine are bent), the fiber cores (highest layer curvature), and the intersector boundaries. When replacement of serpentine by talc is more advanced, sectors become fully pseudomorphed by talc-like lamellae (Figs. 8g and 8h) and talc-like lamellae may develop rounded aggregates, mimicking the rounded shapes of former serpentine particles (Figs. 8i and 8j). It is worth noting that these poorly crystalline, talc-like layers are bent and characterized by extremely wide interlayer partings, giving rise to a highly porous nanotexture (Figs. 5d, 5e, and 8h).

The overall data indicates that the formation of the successive phases in the garnierite mixtures may be explained by an early formation of serpentine tubes. The diameter of the serpentine cores in type II is comparable to the outer diameter of narrow chrysotile tubes in type I. This may indicate that the diameter of the chrysotile increases in size until its curled structure is unstable. Then it is transformed into polygonal serpentine while preserving a cylindrical core, which may more likely be altered by later dissolution-precipitation than polygonal sectors. The serpentine particles are subsequently replaced by “kerolite”-“pimelite”, starting from high stress sites and structural discontinuities, such as cores, rims, and contact between sectors. The final product is possibly a garnierite formed exclusively by talc-like lamellae (Fig. 9).

The later formation of “kerolite”-“pimelite” from serpentine particles is in accordance to the garnierite precipitation model proposed by Gali et al. (2012). This model is based on the assumption 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, then followed by “kerolite”-“pimelite”, and eventually by sepiolite–falcondoite and sepiolite–falcondoite with amorphous silica and/or quartz (Gali et al. 2012).

Implications

The results obtained in this comprehensive TEM study on the garnierites from the Falcondo Ni-laterite deposit (Dominican Republic) reveal that the Ni-bearing serpentine, “kerolite”-“pimelite” and sepiolite-falcondoite components display a wide variety of
Figure 8. Replacement textures between Ni-phylllosilicates. (a) Sectored serpentine being replaced by talc-like lamellae, with talc-like lamellae inside the serpentine core (b) and growing from the serpentine edges (e) (sample LC-100AB-5). (d) Large 15-sectored polygonal serpentine, showing talc-like lamellae inside the core and at the edges of sectors (e) and at the border (f) (sample LC-100AB-5). (g) Polygonal serpentine being altered to talc-like lamellae. (h) Detail of g (sample 09GAR-2.1). (i–j) Rolled talc-like lamellae recording textures of former serpentine particles (i) sample 09GAR-2.1 and (j) LC-100AB-5. All these images were obtained in a Jeol 2010 (UniSi).
Figure 9. Replacement model that may explain the formation of Ni-enriched talc-like (“kerolite”-“pimelite”) lamellae from the alteration of Ni-poor serpentine particles (1a–3a) and HRTEM images representative of each precipitation stage (1b–3b): early formation of polygonal serpentine and chrysotile tubes (1a and 1b), which are subsequently replaced by talc-like lamellae mainly in the higher stress sites (inner cores, outer rims, borders between sectors) (2a and 2b), leading to a complete replacement of serpentine particles by talc-like, leaving some rolled and curved talc-like lamellae as remnants of the former serpentine features (3a and 3b). The HRTEM images were obtained in a Jeol 2010 (UniSi): sample LC-100AB-5 (1b), sample 09GAR-2.1 (2b), and sample LC-100AB-4 (2c).

Table 2. Representative normalized AEM analyses performed on Falcondo garnierites in atoms per formula unit (apfu)

| Sample | Type I (Sr) | Type I (Sr) | Type I (Tlc) | Type I (Tlc) | Type II (Sr) | Type II (Sr) | Type II (Sr) | Type II (Tlc) | Type II (Tlc) | Type III | Type III | Type IV | Type IV | Type IV | Type V | Type V | Type V |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----------|-----------|----------|----------|----------|--------|--------|--------|
|        | LC-101      | LC-101      | LC-101      | LC-101      | LC-100B     | LC-100B     | LC-100B     | LC-100B     | LC-100B     | GAR-2.3B  | GAR-2.3B  | LC-100B  | LC-100B  | LC-100B  | GAR-7v-3 | GAR-7v-6 | GAR-7v-7 |
| O atoms formula | 14 | 14 | 22 | 22 | 14 | 14 | 14 | 22 | 22 | 22 | 22 | 22 | 22 | 32 | 32 | 32 |
| Mg     | 2.737       | 2.509       | 2.374       | 2.111       | 2.756       | 2.556       | 2.590       | 1.482       | 1.008       | 0.364     | 0.417     | 0.413    | 1.440    | 1.494    | 1.725   | 2.138   | 2.013   |
| Al     | 0.000       | 0.000       | 0.000       | 0.000       | 0.266       | 0.094       | 0.000       | 0.000       | 0.000       | 0.000     | 0.000     | 0.000    | 0.000    | 0.000    | 0.000   | 0.000   | 0.000   |
| Si     | 1.825       | 2.085       | 3.869       | 3.846       | 1.888       | 1.899       | 2.132       | 3.905       | 3.907       | 3.770     | 3.757     | 3.966    | 3.997    | 4.015    | 4.026   | 6.065   | 6.106   |
| K      | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000     | 0.000     | 0.000    | 0.000    | 0.000    | 0.000   | 0.000   | 0.000   |
| Ca     | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000     | 0.000     | 0.000    | 0.000    | 0.000    | 0.000   | 0.000   | 0.000   |
| Cr     | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000     | 0.000     | 0.000    | 0.000    | 0.000    | 0.000   | 0.000   | 0.000   |
| Mn     | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000       | 0.000     | 0.000     | 0.000    | 0.000    | 0.000    | 0.000   | 0.000   | 0.000   |
| Fe³⁺   | 0.386       | 0.160       | 0.158       | 0.072       | 0.023       | 0.305       | 0.067       | 0.018       | 0.018       | 3.096     | 3.068     | 3.069    | 3.007    | 2.971    | 2.948   | 3.871   | 3.787   |
| Ni     | 0.035       | 0.080       | 0.651       | 1.091       | 0.035       | 0.047       | 0.045       | 1.681       | 2.070       | 3.770     | 3.757     | 3.966    | 3.997    | 4.015    | 4.026   | 6.065   | 6.106   |
| ΣOcta  | 3.158       | 2.750       | 3.183       | 3.273       | 2.814       | 2.908       | 2.702       | 3.182       | 3.097       | 3.158     | 2.750     | 3.183    | 3.273    | 2.814    | 2.908   | 2.702   | 3.182   |
| ΣTetra | 1.825       | 2.085       | 3.869       | 3.846       | 2.154       | 1.993       | 2.132       | 3.905       | 3.961       | 1.825     | 2.085     | 3.869    | 3.846    | 2.154    | 1.993   | 2.132   | 3.905   |

Table 2. Representative normalized AEM analyses performed on Falcondo garnierites in atoms per formula unit (apfu)
textures and sizes at the nanometer scale. It is worth noting that most of the observed textures in Mg-serpentines (e.g., lamellae, chrysotile tubes, polygonal) are also found in their Ni-bearing analogs. However, the studied samples are characterized by low Ni contents in serpentines, whereas Ni is concentrated in the talc-like phases, reinforcing previous works (Villanova-de-Benavent et al. 2014a, 2014b). The results altogether provide further insight on the mineralogy of Ni-phyllosilicates as the highest grade Ni ores in a world-class hydrous silicate type Ni-laterite deposit.

The most noteworthy result of this work is the first evidence of replacement at the nanometer scale among garnierite-forming minerals. We have demonstrated that the Ni-enriched talc-like lamellae replace the polygonal serpentine and chrysotile tubes in the higher stress sites. In this model the Ni-enriched talc finally replaces the serpentine completely leaving some rolled and curved talc lamellae as remnants of the former serpentine (Fig. 9). This provides the direct proof that the crystallization of the Ni-bearing phyllosilicates at low temperature is associated with an increase in the silica activity of the system, which is coherent with previous observations at the micrometer scale (Villanova-de-Benavent et al. 2014a) and the thermodynamic model for garnierites that predicted that Ni is preferentially contained within the talc-like phase (Gali et al. 2012). As a consequence, Ni-enriched talc phases precipitate from already formed secondary serpentine particles. In the long term, in a more advanced stage of weathering, this will lead to the complete dissolution of serpentine particles that will be entirely substituted by Ni-enriched talc-like and even sepiolite-like phases as the silica and Ni activity increase. In addition it is worth noting that this Ni-enrichment process leads to the formation of remarkable porosity in the material.

Therefore, the results of this work contribute to the knowledge of the formation of Ni-phyllosilicates under tropical conditions demonstrating that the Ni-poor serpentine particles are replaced by Ni-rich talc-like phases. This in turn has interesting implications in the field of material sciences. Recently (i.e., Siviah et al. 2011), synthesized Ni-containing serpentine-like and talc-like phyllosilicates were used as catalyst precursors for processing greenhouse gases (i.e., CO₂, CH₄). Thus the TEM characterization presented in this work also suggests that natural garnierites could be a good candidate to accomplish the requirements of a suitable catalyst precursor.

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