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**Swelling capacity of mixed talc-like/stevensite layers in white/green clay
infillings ('deweylite'/'garnierite') found in serpentine veins of faulted
peridotites (New Caledonia)**

REVISION 2

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Abstract: White (Mg-rich) and green (Ni-rich) clay infillings ('deweylite'/'garnierite') found
in serpentine veins of faulted peridotite formations from New Caledonia consist of an intimate
mixture of fine-grained and poorly ordered 1:1 and 2:1 layer silicates, commonly referred to
as non-expandable serpentine-like (SL) and talc-like (TL) minerals. New data on the swelling
and shrinking capacity of these layer silicates were gathered from X-ray diffraction (XRD)
after saturation of the clay fractions with different cations (Ca²⁺, Li⁺, K⁺), ethylene glycol
(EG) solvation, and heating treatments. Simultaneously, layer charge distribution and vacancy
density respectively were investigated by FTIR spectroscopy on NH₄-saturated clay fractions

and by XRD on Li-saturated clay fractions before and after heating (Hofmann Klemen treatment). Five clay infillings, with dominant 2:1 layer silicates and variable Ni contents, were selected for this study, from a large set of veinlets, according to their swelling capacity. The crystal chemistry of these samples was established from FTIR spectroscopy and bulk chemical analyses.

The swelling ability of the clay infillings is attributed to the 2:1 layer silicates. It does not seem to be affected by the relative fraction of Mg and Ni in their octahedral sheets. On XRD patterns, the swelling ability is linked to a slight shift of the basal reflection of the 2:1 layer silicates towards low angles for bulk samples and to a split of that reflection in two contributions for clay fractions saturated with Ca (or Li) and solvated with EG. The amplitude of the split increases with the swelling capacity of the sample. It originates mainly from octahedral-layer charge generated by vacant sites. Such results lead us to consider the 2:1 layer silicates of the infillings as an intimate mixture of non-expandable (TL) and expandable (stevensite) phases. In agreement with previous studies which suggested a contribution of hydrothermal processes in the alteration of serpentine species into 2:1 layer silicates, we propose that the proportion of expandable phases in the clay infillings (or vacant sites in the octahedral sheets of the 2:1 layer silicates) could be used as an efficient probe for assessing their temperature of formation. Clay infillings mostly made of stevensite would have formed at ambient temperatures, whereas those consisting mainly of non-expandable TL would have formed at higher temperatures.

Introduction

Nickeliferous laterites developed on ultramafic rocks (e.g. dunite, harzburgite) in tropical regions are of particular interest as they commonly contain two kinds of Ni-silicate ores: (1) 'clay silicate' ores, and (2) 'hydrous Mg/Ni silicate' ores (Brand et al., 1998; Gleeson et al.,

2004; Freyssinet et al., 2005; Wells et al., 2009, Fritsch et al. 2016). Layer silicates of the ‘clay silicate’ ores are mostly composed of swelling dioctahedral 2:1 layer silicates (smectite) such as Fe-nontronite, Fe-montmorillonite, and Al-beidellite (e.g. Gaudin et al., 2004). They usually occur in saprolite, at the bottom of thick and poorly drained lateritic profiles developed on ultramafic rocks and correspond to low-grade Ni-deposits (less than 4 wt % Ni). By contrast, layer silicates of the ‘hydrous Mg/Ni silicate’ ores mostly consist of weakly expandable trioctahedral 1:1 and 2:1 layer silicates of the serpentine (unit cell formula: $\text{Si}_2[\text{Mg,Ni}]_3\text{O}_5(\text{OH})_4$) and talc (unit cell formula: $\text{Si}_4[\text{Mg,Ni}]_3\text{O}_{10}(\text{OH})_2$) mineral groups (e.g. Brindley and Hang, 1973; Brindley and Wan, 1979, Brindley, 1980; Manceau and Calas, 1985; Tauler et al., 2009; Wells et al., 2009). Because of their small size and low crystal order (stacking defects and vacancies), these layer silicates are commonly referred to as serpentine-like (SL) and talc-like (TL) minerals (Villanova-de-Benavent et al., 2014; 2019; Fritsch et al., 2016). Because of similar ionic charge and ionic radius, Ni (0.69 Å) can replace Mg (0.72 Å) in the octahedral sites of trioctahedral clay minerals leading to various mineral series with large ranges in chemical composition (Faust, 1966, Faust and Murata, 1953, Brindley et al., 1977). Mineral associations of trioctahedral 1:1 and 2:1 clay minerals in veinlets are termed deweylite for the white Mg-rich phases (Bish and Brindley, 1978) and garnierite for the bluish green Ni-rich phases (Pecora et al., 1949). Kerolite is the magnesium-rich end-member, while pimelite is the nickeliferous end-member for the TL mineral series. Such layer silicates are present at depth in white (deweylite) to green (garnierite) clay infillings of faulted saprock and observed in both freely and poorly drained lateritic profiles (Cluzel, 2006; Cluzel and Vigier 2008; Fritsch et al., 2016; 2019; Villanova-de-Benavent et al., 2014). They are widely observed in peridotite massifs of New Caledonia and are related to high-grade Ni-deposits (up to 32 wt % Ni).

The two kinds of silicate ores are therefore associated with contrasting geochemical and structural environments, which suggest that they might have formed under distinct weathering (or alteration) conditions. Whereas the ‘clay silicate’ ores are commonly associated with the vertical development of thick lateritic profiles under poorly drained conditions (e.g. Gaudin et al., 2004), recent studies in New Caledonia suggest that the ‘hydrous Mg/Ni layer silicate’ ores might have formed in reactivated faults from the hydrothermal alteration of serpentine species into TL minerals during the dismantling and cooling of the ophiolite nappe (Fritsch et al., 2016; 2019; Cathelineau et al., 2017). Hydrous Mg/Ni layer silicates were described elsewhere in different climatic environments but in similar geological settings, for example in serpentinite at structural contacts in Greece (Christidis and Mitsis, 2006) and in Italy (Capitani and Ventruti, 2018).

Detailed textural and mineralogical investigations on the serpentinitised and mineralised faults show that minerals of the serpentine group are predominant at the margin of the veins, whereas those of the talc group prevail in association with quartz in their central part (Christidis and Mitsis, 2006; Fritsch et al., 2016, 2019). In addition, TL minerals have locally been described in association with stevensite (Brindley and Hang, 1973, Wiéwióra et al., 1982) or as mixed layers stevensite-talc (Eberl et al., 1982; Christidis and Mitsis, 2006). Stevensite is considered a swelling trioctahedral (Mg, Ni) 2:1 layer silicate (smectite) with a chemical composition similar to that reported for TL minerals but with vacant sites in its octahedral sheets (Christidis and Mitsis, 2006). Scarcely reported worldwide, this swelling phase has most likely been overlooked in recent mineralogical studies on Ni-laterite deposits (Villanova-de-Benavent et al., 2014; 2016; 2019; Fritsch et al., 2016; 2019; Cathelineau et al., 2016; Capitani and Ventruti, 2017; Tauler et al., 2017; Munoz et al., 2019).

This paper describes, for the first time, the occurrence of stevensite in vein-infillings of reactivated faults from peridotitic formations of New Caledonia. Five samples of white

(deweylite) and bluish green (garnierite) clay infillings, with distinct swelling abilities, were selected from a large set of vein infillings to investigate the relationship between swelling capacity, crystal-chemistry, charge deficiency, and structural disorder (stacking defects and vacancies). Our results aim at deciphering the mechanisms involved in these changes of swelling and crystallographic properties in order to better understand the conditions of formation of the hydrous Mg/Ni layer silicates.

Materials and Methods

The five samples investigated in this study (Figures 1 and 2) belong to a large set of clay infillings, whose texture, mineralogy and chemistry were established in previous works (Fritsch et al. 2016, 2019). They were collected at depth in the saprock, more specifically, in fractures of highly serpentinised zones of two peridotite formations (mainly harzburgite) of the New Caledonian mainland (Figure 1): (i) the Koniambo klippe (mining site “Manguen”) on the Western coast (MG1aWill, MG3aWill) and (ii) the Poro klippe (mining site “La Française” of the CFTMC) on the Eastern coast (BONBR2a, BONBR2c, LFSTA5a2). Both klippees are known for an abundance of fractures and associated crosscutting mineralised veins (also named box-works or “Minerai quadrillé” in the French literature), which grade from white (deweylite) to bluish green (garnierite) according to the relative proportion of Mg and Ni. The five samples selected for this study belong to an ultimate episode of clay infillings predominantly made of 2:1 layer silicates (see Fritsch et al. 2016 for a more detailed description of the vein-infillings). They were selected according to their ability to swell and shrink. Shrinking in the field leads to the development of cracks along the clay infillings after exposure of the mining cuts to air (Figure 2b). On thin sections it is also related to the

occurrence of a dense network of cracks, more specifically in Ni-rich bands of the infillings (Figure 2d).

Samples were air-dried and crushed with a pestle and mortar before chemical and mineralogical investigations. Chemical analyses of the samples were carried out by digestion of 1000 mg of the finely powdered sample in a high-pressure TFM Teflon vessel using an ETHOS 1600 MILESTONE microwave system, with samples digested using a mixture of 3mL of HCl (37%), 2mL of HNO₃ (65%), 1.5mL of HF (40%) and 5mL of H₃BO₃ (5%). After digestion the solution was diluted with osmosed water. Si, Mg, Ni, Co, Al, Fe, Ca, Cr and Cu concentrations were determined using a Perkin Elmer 1100b atomic absorption spectrophotometer. Loss on ignition (LOI) was determined after heating at 1000°C without pre-drying at 105°C.

To determine the clay (<2 µm fraction) mineralogy, bulk samples were gently ground in agate mortar and sieved at 50 µm. The < 50µm fractions were dispersed into 1 mol L⁻¹ NaCl and by ultrasonication. This procedure was reproduced five times to ensure complete Na saturation and dispersion of the samples. The clay fractions were then obtained by centrifugation according to the Stokes' law. The suspended clay fractions were flocculated with 0.5 mol. L⁻¹ CaCl₂ and divided into aliquots for saturation with different cations (Ca²⁺, K⁺, Li⁺ and NH₄⁺). The aliquots were treated five times with 0.5 mol. L⁻¹ CaCl₂, and 1 mol. L⁻¹ KCl, LiCl, and NH₄Cl, and washed with osmosed water to remove excess salts until a negative test with 1 M AgNO₃ was obtained. As Li⁺ and NH₄⁺ may enhance dispersion and formation of gels, the Li- and NH₄-saturated samples were washed in ethanol instead of osmosed water and ultra-centrifuged (30000 g). K-saturated samples were heated at 20, 150, 350 and 550°C and examined by XRD. Ca-saturated and Li-saturated samples were analysed by XRD both in an air-dried (AD) state and after ethylene glycol solvation (EG, vapour at 50°C overnight) to assess the swelling capacity of the layer silicates. The Hofmann-Klemen (HK) treatment

(Hofmann and Klemen, 1950; Greene Kelly, 1953, 1955) was also applied to the five clay samples to reveal the possible occurrence of octahedral vacancies in clay minerals. The Li-saturated samples were heated overnight at 300°C to induce migration of Li⁺ into octahedral vacancies of the phyllosilicates. For trioctahedral smectites the swelling behaviour of the layers after HK treatment depends on the location of the charge. When the charge originates from the octahedral sheet, the Li saturation and heating implies only partial neutralisation of the charge by migration of a monovalent cation (Li⁺) in the octahedral vacancy, and the layers may remain expandable in EG (Petit et al., 2008, Gaudin et al., 2004) or glycerol (Brindley and Brown, 1980). Oriented clay mounts were obtained by dropping a small amount of clay suspensions onto glass slides (or zero background Si wafers) and drying them at room temperature. For some preparations the suspensions were made in ethanol to avoid the formation of gels.

Bulk mineralogy of samples was determined by XRD on randomly oriented powders in the step scan mode in the range 2–65° 2θ with steps of 0.025° 2θ and a counting time of 229s per step using a Bruker D8 Advance diffractometer (Cu Kα radiation, 40kV and 40mA) equipped with a Lynx eye detector. XRD patterns of oriented preparations were recorded in both AD and EG solvated states in the step scan mode in the range 2–35° 2θ with steps of 0.016° 2θ and a counting time of 229s. Background stripping was carried out on XRD patterns of oriented preparations and the 00*l* diffraction peaks of the layer silicates were decomposed into Gaussian curves with Fityk® (Wojdyr, 2010) to determine peak positions, peak areas, and full width at half maximum (FWHM), the latter being converted into coherent scattering domain sizes (CSDS) in the *c* direction (defined by the statistical range of number of layers: *N*).

Fourier transform infrared (FTIR) spectra of bulk and <2μm samples were recorded in the middle IR 400–4000 cm⁻¹ range (MIR) using a Nicolet 760 FTIR spectrometer in transmission mode with a 4 cm⁻¹ resolution. The spectrometer was continuously purged with dry, CO₂-

depleted air. MIR spectra were recorded from disks prepared by mixing 1 mg of the sample with 150 mg of KBr and pressing them at 10 tons.cm⁻². Pellets were heated overnight at 110°C to remove absorbed water before the FTIR spectra were recorded. Layer charge distribution, (i.e. tetrahedral (Te), octahedral (Oc) and variable charges), was estimated by quantifying the amount of NH₄⁺ fixed by the samples, before and after Li-saturation and heating at 300°C, using the integrated intensity of the ν₄NH₄ band at 1400 cm⁻¹ of normalised FTIR spectra (Petit et al., 1998, 2002, 2008; Gaudin et al., 2004, Mano et al., 2014). The NH₄⁺ fixed by the swelling layers of the raw samples corresponds to the total charge of the layers (permanent [Te + Oc] + variable edge charges). It is considered as the CEC at the pH of the NH₄Cl solution. After Li saturation and heating at 300°C (HK test), the amount of NH₄⁺ fixed by the layer silicates corresponded to the remaining charge, not neutralised by migration of Li⁺ in the octahedral sites (Petit et al., 1998, 2006). FTIR spectra of the NH₄⁺-saturated samples (NH₄⁺ and Li₃₀₀NH₄⁺) were recorded using the same amount of clay and normalised to the OH vibration bands of the main SiO band around 1020 cm⁻¹. Near infrared (NIR) spectra were recorded at a resolution of 4 cm⁻¹ from 4000 to 10,000 cm⁻¹ in a glass vial, with a Thermo Scientific Integrating Sphere (diffuse reflectance) with an internal InGaAs detector coupled to a Thermo Scientific Nicolet 6700 FT-IR spectrometer.

RESULTS

Mineralogy and crystal-chemistry

Mineralogy and crystal-chemistry of hydrous Mg/Ni layer silicates from the five samples selected for this study were established from XRD (Figures 3, 6 and 9), FTIR spectroscopy (Figure 4, Table 2), and bulk chemical analyses (Table 1, Figure 5). XRD patterns and FTIR

spectra are stacked in the figures according to the ability of the samples to swell (the less expandable at the bottom and the more expandable at the top).

Bulk mineralogy

In agreement with previous studies carried out on a larger set of mineralised veins (Fritsch et al. 2016), powder XRD patterns of bulk samples (Figure 3) show that the clay infillings of the samples consist of a mixture of 7 Å-type (1:1) layer silicates of the serpentine mineral group (peaks at 7.32 to 7.38 Å and 3.64 to 3.66 Å) and 10 Å-type (2:1) layer silicates of the talc mineral group (peaks at 10.01 to 11.12 Å and at 3.20 to 3.22 Å). The powder XRD pattern of the less expandable sample (MG1aWill) also displays quartz (Qz). According to XRD results, sample BONBR2c, which is free of Ni (white color), is the richest in SL components and contains TL minerals with poorly resolved *001* reflection. Conversely, powder XRD patterns of samples with greater Ni contents (bluish green colours) present better resolved *001* reflection for TL minerals and smaller proportions of serpentine. The position at ~ 1.525 Å for the shared 06-33 reflection of 1:1 and 2:1 layer silicates indicates that all samples consist of pure tri-octahedral clay minerals with a dominance of bivalent cations (Mg^{2+} and Ni^{2+}) in the octahedral sheets (Table 1, Figure 3).

The broad basal *001* reflections and the presence of two-dimensional hk bands (20-13) attest to small coherent scattering domain sizes (CSDS), and structural disorder (stacking defects and vacancies) that enable to refer the layer silicates to serpentine-like (SL) and talc-like (TL) minerals (Brindley and Hang, 1973; Brindley et al., 1977; Bish and Brindley, 1978; Brindley and Brown, 1980; Decarreau et al., 1987; Proenza et al. 2008; Tauler et al., 2009; Villanova-de-Benavent et al., 2014; Fritsch et al. 2016). On the powder XRD patterns of the less expandable (MG1aWill) and the most expandable (BONBR2c) samples, the sharp reflection at ~ 2.51 Å (and to a lesser extent that at ~ 2.45 Å) is superimposed to the broad 20-13 band

(Figure 3). These sharp reflections, on broader reflections of cryptocrystalline SL and TL, suggest additional occurrence of crystalline serpentine (Srp) as reported by Fritsch et al. (2016) on XRD patterns (reflection at 2.51 Å for lizardite 1T and 2.45 Å for chrysotile 2M) and on HR-TEM images (large platelets of lizardite and tubular shaped chrysotile). These variations are also consistent with the presence of a peak asymmetry on the low-angle side of the basal reflections. For the most expandable sample (BONBR2c), the first basal reflection of the 7 Å layer silicates was fitted with two Gaussians (not shown): (i) a first one with a narrow reflection at 7.32 Å (CSDS: 60-75 *N*) which is attributed to well-crystallised serpentine residues (Srp) and (ii) a second wide one at 7.38 Å with smaller CSDS (15 *N*) corresponding to poorly ordered SL species (Fritsch et al., 2016). The statistical range of the number of layers (*N*) can vary widely for the 1:1 layer silicates (from 75 to 15), according to the amount of serpentine residues (Srp) in the samples. By contrast, the CSDS value is systematically smaller for the 10 Å-type layer silicates ($8 < N < 18$), thereby underlining the small size of the poorly crystallized TL minerals.

Mg and Ni speciation in the layer silicates

FTIR spectra (Figure 4) confirm the mineral composition of the samples (mostly made of TL and SL minerals) and reveal the distribution of divalent cations (Mg and Ni) in the octahedral sites of the layer silicates (Farmer, 1974; Gerard and Herbillon, 1983; Balan et al., 2002; Petit, 2005; Christidis and Mitsis, 2006; Jagannadha Reddy et al., 2009; Mano et al., 2014; Baron and Petit, 2016; Baron et al., 2016). In the white and Ni-free clay sample (BONBR2c), the 3697 cm⁻¹ and 3650 cm⁻¹ bands of the MIR spectrum belong to serpentine species (Figure 4a). They were assigned respectively to the inner OH stretching and the out-of-phase vibrations of the inner-surface OH of lizardite (Balan et al. 2002). On the same spectrum, the band at 3677 cm⁻¹ can be assigned to OH stretching vibrations in $\nu\text{Mg}_3\text{OH}$ configuration of

TL (e.g. Baron et al. 2016). These assignments imply that the bands observed at 7239 cm^{-1} and 7185 cm^{-1} on the NIR spectrum of BONBR2c correspond to second overtone vibrations ($2\nu\text{Mg}_3\text{OH}$) in SL and TL minerals, respectively. The other bands reported at lower frequencies on the MIR and NIR spectra of the four bluish green clay samples (BONBR2A, MG3aWil, LFSTA5a2 and MG1aWil) most likely result from additional occurrence and distinct distribution of Ni in octahedral sheets of these layers silicates. More specifically, the 3628 cm^{-1} (MIR – Figure 4a) and 7081 cm^{-1} (NIR – Figure 4b) bands are respectively assigned to first and second overtones Ni_3OH stretching for TL minerals and trioctahedral smectites (Farmer, 1974; Gerard and Herbillon, 1983; Petit, 2005; Christidis and Mitsis, 2006; Jagannadha Reddy et al., 2009; Mano et al., 2014; Baron and Petit, 2016; Baron et al., 2016). The 3650 cm^{-1} (MIR – Figure 4a) and 7125 cm^{-1} (NIR – Figure 4b) bands can also be attributed to first and second overtones MgNi_2OH stretching for TL minerals (Petit et al., 2004; Baron and Petit, 2016). As highlighted by Fritsch et al. (2019), these results suggest that TL minerals (and/or trioctahedral smectite) are the main Ni-bearing phases of the Ni-silicate ores. Nevertheless, the bands at 3650 cm^{-1} (MIR) and 7125 cm^{-1} (NIR) could also be assigned to $\nu\text{Ni}_3\text{OH}$ in serpentine (Baron et al., 2016). These bands are commonly poorly resolved, except for sample MG1aWill, which could therefore contain Ni-rich SL minerals (Nepouite) in addition to Ni-rich TL minerals (Pimelite).

Chemical composition

Bulk chemical compositions of the five samples (expressed in oxide weight %) are listed in table 1. These layer silicates are mainly composed of Si with minor Fe, highly variable Mg, and Ni contents (or reverse Mg and Ni variations), and are free of Al. Bulk chemical data converted to number of atoms and plotted in a ternary $\text{Si}/(\text{Mg}+\text{Fe})/\text{Ni}$ diagram (Figure 5) reveal that all five samples are within a triangle delineated by the Mg/Fe end-member of

serpentine species (Srp), and the Mg and Ni end-members of talc (Tlc). As outlined by Fristch et al. (2016; 2019), the relative proportion of TL minerals in mixtures of both 7 Å and 10 Å layer silicates can be assessed from the mole Si:ΣR ratio (with ΣR = Mg+Fe+Ni). This ratio is shown on the ternary diagram by a horizontal line. Theoretically, it ranges from 2/3 in samples composed exclusively of serpentine species $[R_3Si_2O_5(OH)_{4-n}H_2O]$ to 4/3 in those composed only of 2:1 layer silicates in the talc mineral group $[R_3Si_4O_{10}(OH)_2]$ (see the two horizontal solid lines in Figure 5). The ternary Si/(Mg+Fe)/Ni diagram shows, therefore, that the five samples present dominant TL minerals in the mixture of 7 Å and 10 Å layer silicates, which is consistent with Si:ΣR ratios greater than 1.00. This is consistent with XRD patterns showing a major contribution of the basal reflections of the 2:1 layer silicates compared to those of the 1:1 layer silicates (Figure 3). Samples with the highest Si/ΣR ratios and lowest Fe contents (Table 1) are predominantly made of TL minerals and are, therefore, the closest to the theoretical line for talc on the ternary diagram. This is the case for samples MG1aWill and MG3aWill. The presence of quartz in MG1aWill, in addition to TL minerals, as highlighted by XRD, may also increase the Si/ΣR and thus induce an overestimation of the proportion of TL minerals. Major chemical changes are related to a right shift of the data from the Mg+Fe pole to the Ni pole of the ternary diagram. In agreement with our IR data, this shift points to a gradual increase of the Ni for Mg substitution in the layer silicates (mostly TL minerals) of the infillings. This substitution rate is nil in the most expandable sample (BONBR2c) and optimal in the less expandable sample (MG1aWill).

Swelling and shrinking behaviour

XRD patterns of oriented mounts of the < 2 µm fraction of the five samples saturated with Ca or Li in AD and EG states are given in Figure 6. XRD patterns of the Ca-saturated samples in AD state are very similar to the XRD patterns of the powder bulk samples (Figure 3). They all

present similar peak position and broadening of the basal $00l$ reflections characteristic of poorly crystalline 1:1 (SL) and 2:1 (TL) layer silicates. The position of the $00l$ reflection of the 2:1 layer silicates in AD state ranges from 9.92 Å (MG1aWill) to 10.20 Å (BONBR2c) for the Ca-saturated samples (Figure 6a, Table 2) and from 9.92 Å (MG1aWill) to 10.82 Å (BONBR2c) for the Li-saturated samples (Figure 6b, Table 2). The position of this reflection at about 10 Å is slightly greater than that generally reported at 9.6 Å for non-expandable TL minerals (Brindley et al., 1977).

XRD patterns of the Ca or Li-saturated samples in EG state (Figure 6) show no significant change of peak position for the 1:1 layer silicates (Srp and SL), indicating an absence of swelling phase (Figure 6). The $00l$ reflection of the 2:1 layer silicates for MG1aWill is at the same position (~ 10 Å) in the AD and EG states confirming also the absence of swelling phase (Figures 6 and 7; Table 2). The most expandable sample (BONBR2c) exhibits a $00l$ peak of 16.47 Å for CaEG and 17.04 Å for LiEG, and a 002 peak of ~ 8.80 -8.90 Å for CaEG and LiEG (Figures 6 and 7; Table 2). These harmonic peaks are close to that reported by Christidis and Mitsis (2006) for stevensite (respectively 17.6 Å and ~ 9.02 Å). The other samples have intermediate amounts of expandable and non-expandable layers, according to the position of the first basal reflection between 10 and 17 Å in EG state. Figures 6a and 6b also show that EG solvation of the two most expandable samples, BONBR2a and BONBR2c, saturated with Li^+ leads to greater resolution of reflections, as well as to a greater shift of the peaks towards low angles (i.e. larger d-spacing) than for samples saturated with Ca (Table 2). Such differences likely result from the smaller size of Li^+ and different ionic potential compared to Ca^{2+} , implying different solvation behaviours with water or ethylene glycol.

The swelling and the splitting of the $00l$ reflection in samples BONBR2a, BONBR2c and MG3aWill are better illustrated in background stripped patterns (Figure 7). The asymmetric $00l$ reflection at ~ 10.0 Å for the 2:1 layer silicates in AD state (dots in Figure 7) can be fitted

with two overlapping Gaussian curves (dashed lines, Figure 7). The peak asymmetry disappears with EG solvation and is replaced by two contributions, which are fitted with two separate Gaussian curves (plain line). From bottom to top of Figure 7, the increase of the swelling ability of the three samples is linked to a shift of the first contribution (P1) towards low angles (14.15 Å for MG3aWill, 15.27 Å for BONBR2c and 17.04 Å for BONBR2a) with a concomitant increase of the peak area. On the opposite, the second contribution (P2) shift towards greater angles (9.44 Å for MG3aWill, 9.24 Å for BONBR2c and 8.83 Å for BONBR2a) and gradually collapse. These variations suggest therefore a random interstratification (R0) between swelling (smectite) and non-swelling phases (TL) with a variable proportion of the two components.

Figure 8 displays the positions of both contributions (P1 and P2) for the five Ca- and Li-saturated samples in EG state. The progressive variation of the P1 and P2 positions from samples MG1aWill to BONBR2c suggests a continuum between the non-expandable TL and the fully expandable smectite. It also shows that the P1 and P2 positions are negatively correlated and that non-expandable TL minerals and stevensite are present at the extremities of the trend. More specifically, P1 and P2 are merged and located close to the *001* reflection of the non-expandable TL minerals (corresponding to a d-spacing of ~ 9.6 Å) in the non-swelling sample (MG1aWill) and widely dissociated and positioned close to the *001* (P1) and *002* (P2) reflections of stevensite (d-spacing close to 17.6 Å and 8.8 Å, respectively) in the highly swelling sample (BONBR2c). Accordingly, the position of both reflections (P1 and P2) could be used to assess the relative proportion of swelling layers (stevensite) in the pool of the 2:1 layer silicates.

Following K-saturation and gradual heating from room temperature to 550°C, the *001* reflection of TL was displaced from 10.0-9.9 Å to 9.6-9.7 Å (Figure 9). Simultaneously, the intensity and width of the d_{001} peaks, as well as the asymmetry on the low angle side,

decreased with increasing heating for all samples except MG3aWILL. These variations indicate a preferential collapse of the swelling (or hydrated) layers of these clay minerals. The position of the 001 reflection at ~ 9.6 Å after heating and the destruction of the swelling layers therefore reveals the non-expandable TL minerals (Brindley et al., 1977). At 550 °C the collapse of the 001 reflection is complete for serpentine (thermal dehydroxylation of Srp and SL minerals) whereas it remains partial for TL minerals.

Layer charge and vacancies

XRD patterns of the Li-saturated samples after heating at 300°C (Hofmann Klemen treatment) show a peak displacement from 10.87 Å (LiAD) to 10.44 Å (Li₃₀₀) for BONBR2c and from 10.07 Å (LiAD) to 9.93 Å (Li₃₀₀) for MG1aWill (Li₃₀₀, Figure 6b). For the five samples the intensity of collapse is related to the proportion of swelling layers. Following EG solvation after HK treatment (Li_{300EG} Figure 6b) the 001 and 002 peaks are broad and hardly discernible from the background for samples BONBR2a, BONBR2c and LFSTA5a2, and their position ranges from ~ 15 Å to ~ 17 Å and from ~ 9.4 Å to ~ 8.8 Å, respectively. This behaviour indicates that the layer charge is partially neutralised by migration of Li⁺ ions toward vacant sites upon HK treatment, and thus that it originates from the octahedral sheet. The comparison of the FTIR NH₄ band before and after the HK treatment (i.e. NH₄⁺-saturated samples previously saturated with Li and heated at 300°C: Li₃₀₀NH₄) reveals a charge loss that ranges from 63% in the highly expandable sample (BONBR2c) to 39% in the non-expandable one (MG1aWill; Table 3). Upon Li-saturation the samples with the highest swelling ability show the largest charge loss, whereas those with the lowest swelling capacity show the lowest loss of charge neutralised by Li⁺. The swelling ability is thus correlated with the amount of charge neutralised by Li⁺ and hence with the amount of octahedral vacancies. The swelling components of these samples can thus be identified as trioctahedral 2:1 layers

with octahedral vacancies, and therefore as stevensite layers. The decreasing of swelling ability after HK treatment indicates a loss of layer charge due to partial neutralisation of the charge of the stevensite by Li^+ after heating. This is consistent with what is expected for trioctahedral smectites with octahedral charge where Li-saturation followed by heating (HK treatment) induces partial neutralisation of approximately half of the charge (Li^+ vs. R^{2+} ; Petit et al., 2008).

DISCUSSION AND CONCLUSIONS

Swelling capacity and octahedral vacancies of hydrous Mg/Ni layer silicates

The hydrous Mg/Ni layer silicates found in clay infillings of faulted peridotites have recently been related to the early alteration of serpentine veins and conversion of serpentine species into cryptocrystalline SL residues and newly formed TL minerals (Fritsch et al., 2016). These tri-octahedral layer silicates of the serpentine and talc mineral groups have often been considered as non-expandable and the occurrence of swelling layers (i.e. stevensite) has scarcely been reported worldwide (Christidis and Mitsis, 2006; Capitani and Ventruti, 2018). Our work suggests that such occurrence could be more systematic than initially considered. It links the swelling capacity of the samples to the content of stevensite layers (or octahedral vacancies) in the pool of the 2:1 layer silicates of the clay infillings, using XRD and FTIR investigations on clay saturated samples (Ca^{2+} , Li^+ , NH_4^+ , K^+) submitted or not to ethylene glycol and heating treatments.

Swelling of the 2:1 layer silicates is related on XRD patterns of Ca- or Li-saturated and air-dried clay samples to a shift towards low angles of their 001 basal reflection (or development of a peak asymmetry or shoulder on the low angle slopping side of that reflection), and to a

split of this reflection in two contributions (P1 and P2) after solvation of the saturated clay samples with ethylene glycol. The amplitude of the split increases with the swelling capacity of the samples. It is nil ($P1 = P2$) in samples composed of non-expandable TL minerals (001 peak close to 9.6 \AA) and optimal in samples composed exclusively of stevensite within the pool of the 2:1 layer silicates, (P1: 001 peak at $\sim 17.0 \text{ \AA}$, P2: 002 peak at ~ 8.8). Intermediate values for P1 and P2 between these two poles (Figure 8), together with considerable peak width and irrational basal reflections point to the presence of random interstratification (R0) between non-expandable TL and expandable stevensite. These intermediate values could also be due to three-component mixed layers (Figure 10) including non-expandable TL layers, partially expanded stevensite (one sheet of EG), and fully expanded stevensite (two sheets of EG) (Eberl et al., 1982; Christidis and Eberl, 2003).

In this study we also closely linked the swelling behaviour of the clay infillings to layer charge and octahedral vacancies in the 2:1 layer silicates (Hofman Klemen test). As illustrated on figure 10, larger d-spacings (or hydration) in stevensite layers originate from larger numbers of vacant sites in the octahedral sheets and divalent cations (Mg^{2+} , Ni^{2+}) in the interlayer spaces. The non-expandable layers with a low charge are assigned to TL (unit cell formula: $\text{Si}_4[\text{Mg}, \text{Ni}]_3\text{O}_{10}(\text{OH})_2, n\text{H}_2\text{O}$; Figure 10a). Conversely, the fully expandable layers with higher charge and optimum octahedral vacancies are assigned to stevensite (unit cell formula: $(\text{Mg}^{2+}, \text{Ni}^{2+})_x\text{Si}_4[\text{Mg}, \text{Ni}]_{3-x}\square_x\text{O}_{10}(\text{OH})_2, n\text{H}_2\text{O}$ with \square being a random vacancy; Figure 10 b and c). In stevensite, a fraction of divalent cations (Mg^{2+} and Ni^{2+}) no longer occupy octahedral sites, but inter-layer positions (exchangeable cation). Petit et al. (2008) showed for synthetic Zn-stevensite that layers having a charge $< \sim 0.2$ (per half unit cell) are non-expandable while layer having a charge $> \sim 0.2$ (per half unit cell) can swell upon ethylene glycol solvation.

The proportion of Ni in the octahedral sheets of the 2:1 layer silicates (or Ni for Mg substitution rate) does not seem to affect the swelling capacity of these minerals. Although the richest Ni-sample (MG1aWill) contains only non-expandable TL and the Ni-free sample (BONBR2c) mostly stevensite in the pool of the 2:1 layer silicates, the relationship between the Ni for Mg substitution rate and swelling capacity of the 2:1 layer silicates is not as obvious with the other samples (BONBR2A, MG3aWil, LFSTA5a2). On the other hand, Fritsch et al. (2019) reported an opposite trend based on the relationship established on thin sections between the Ni content and anisotropy of the TL infillings. Indeed Mg-rich domains in these clay infillings (kerolite) are commonly anisotropic and observed as botryoidal-shaped ribbons, whereas Ni-rich domains of the same infillings (pimelite) are optically isotropic and cryptocrystalline. This suggests greater amounts of crystal defects (including octahedral vacancies) in pimelite (Ni-rich) compared to kerolite (Mg-rich), which is supported on thin sections by the larger development of cracks in the Ni-rich parts (or bands) of the TL infillings (Figure 2d). Accordingly, further investigation should be undertaken on a larger set of clay infillings to better establish the relationships between Ni for Mg substitution and vacancies in TL minerals.

Conditions of formation

Recent mineralogical and chemical studies on the white and green clay infillings (deweylite/garnierite) found at depth (saprock) in reactivated faults of peridotite formations from New Caledonia have suggested the contribution of temperature and pressure (i.e. hydrothermal processes) in the alteration of serpentine veins into clay infillings predominantly made of TL minerals (Fritsch et al., 2016, 2019; Cathelineau et al., 2017). More precisely, Fritsch et al. (2019) emphasised that temperature in the clay infillings could have affected the size and crystallinity of the 2:1 layer silicates that we assign in this work to

TL minerals, interstratified TL/stevensite and stevensite. On the other hand, laboratory experiments carried out by Decarreau et al. (1987) have shown that the stability fields of talc, kerolite and Mg or Ni-stevensite are temperature-dependent. Stevensites can be synthesised below 100°C, kerolites between 100 and 170°C, and talc at higher temperatures (above 500°C). We conclude then that the proportion of stevensite (or vacant sites) in the pool of the 2:1 layer silicates could be used as an efficient probe for assessing their temperature of formation. Vein infillings exclusively composed of non-expandable TL as 2:1 layer silicates would have precipitated well above 100°C, whereas those composed of almost pure stevensite would have formed below that temperature (i.e. closer to ambient temperature). This interpretation suggests that temperature could have controlled the distribution of non-expandable TL and expandable stevensite along reactivated faults during the early alteration of the peridotite formations. Both mineral phases would have precipitated simultaneously but at different places along the fault network. However, stevensite could also have been produced later during the interaction of meteoric fluids with faulted peridotites and the development of thick lateritic profiles by weathering and hydration of TL minerals into poorly ordered and highly swelling smectite.

Some possible technological implications

Nickel is widely used in industry, because of its chemical and physical properties and resistance to corrosion, for the production of stainless steel, alloys and plating (~70% of Ni consumption), for the production of electric batteries (~30% of Ni consumption), and to a lesser extent as a catalyst. The demand for Ni increases at a rate of ~4 % per year and it will continue to rise in the near future with the development of electrical vehicle/batteries. Nickel is mainly exploited from sulphide and lateritic ores which respectively correspond to 30-40%

and 60-70% of the world resource (Schnebele, 2017). Sulphide ores with high Ni grades have been the dominant source of Ni because processing is simple and cheaper than for laterites. In the recent years, the proportion of Ni extracted from sulphide ores gradually decreased (currently 60-65% of Ni production) with the rarefaction of these deposits (Bergmann, 2003; Gleeson, et al., 2003; Dalvi et al., 2004; Butt and Cluzel, 2013), while that of lateritic ore increased (currently 35-40% of Ni production) and will continue to rise. Because of the progressive decrease in the Ni grade of available laterite ores, the environmental issues, and to help the economically co-exploitation of associated trace metals (e.g. Co in limonitic ores), industrial processes of Ni extraction are becoming more and more complex. Pyrometallurgical processes are predominant for sulphides but the use of hydrometallurgical processes, such as Acid Leaching (AL) or High-Pressure Acid Leaching (HPAL) is increasing for both sulphide and laterite ores (Diaz et al., 1998, McDonald and Whittington, 2008; Rice, 2016; Ucyildiz and Girgin, 2017, Mano et al., 2019). These processes work better for low-grade ores and have better Ni, and other metal, recoveries. To improve these processes, detailed knowledge of the actual mineralogy and crystal-chemistry of Ni-bearing clay silicates is becoming more and more mandatory for economically viable (Ni recovery) and environmentally sustainable (acid consumption) Ni mining.

There is also an increasing interest in the use of Ni-bearing phyllosilicates as catalysts because Ni is one of the most active metals for the dry reforming of methane (activation of C-H bond) and the cleavage of C-C bonds (Wang et al., 1998; Vogels et al., 2005; Iwasa et al. 2006; Sivaiah et al., 2010; Yoshida et al. 2015; Akri et al., 2017). These Ni-clays can be natural or easily synthesised (Iwasa et al. 2006, Baron et al., 2016). The Ni-based catalysts are reduced to between 500 and 800 °C to produce active metal Ni. The Ni content of the Ni-phyllosilicates, their crystal-chemistry (octahedral vs. exchangeable Ni) and resistance to temperature are key parameters in the catalytic efficiency.

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Table captions

Table 1: Chemical analyses of the five samples.

Table 2: Peak position (in Å) of the < 2 µm fraction after saturation with Ca or Li in AD and EG states. For EG state the position of the peak at low angle (P1: 4-7 °2θ) and at high angle (P2: 7-10 °2θ) are given.

Table 3: Estimation of the layer charge loss of the samples using NH₄⁺ saturation and measurement of the area of the band at 1400 cm⁻¹ on MIR spectra before and after Li saturation and heating.

Figure captions

Figure 1: Peridotite formations of New Caledonia and location of the sampling sites for the Mg/Ni silicate ores of the Koniambo and Poro massifs (arrows).

Figure 2: (a) General view of reactivated cross-cutting faults with white (Dew: deweylite) and bluish green (Gar: garnierite) coatings (or infillings) along black serpentine network of saprock (SR_{HZ}) of thick Ni-lateritic profiles (Poro, Fatma), (b) Close up of (a) showing olive green (STL) and turquoise (TL) infillings of a garnierite vein (Gar) with numerous cracks (note also at the periphery of the vein remains of black serpentines and in its central part a thin white silica infilling, Qz), (c) Densely cracked turquoise (sample BONBR2a) and white infillings (sample BONBR2c) along serpentine veins (Srp) of hazburgite saprolite (SAP_{HZ}), (d) BSE image of a garnierite vein showing the whole sequence of clay (STL, TL) and silica

(Qz) infillings. In this vein, the development of cracks (due to drying) is mostly observed in the Ni-rich (light grey) part of the TL infilling.

Figure 3: XRD patterns of randomly oriented powders of the five samples showing broad diffraction peaks of the serpentine-like (SL – 1:1) and talc-like (TL – 2:1) mineral phases and sharp and smaller peaks for residual serpentine species (Srp: mainly lizardite Lz and chrysotile Ctl) and quartz (Qz).

Figure 4: FTIR spectra of the $< 2 \mu\text{m}$ fractions of the five samples **(a)** in the OH-stretching region (Middle Infrared) and **(b)** in the first OH overtone region (Near Infrared) of the 1:1 and 2:1 layer silicates.

Figure 5: Plot of the molar chemical composition of the five samples selected for this study (arrows) (see also table 1 for the chemical composition of the five samples in oxides wt %) in a ternary Si vs Mg+Fe vs Ni diagram within the set of samples investigated by Fritsch et al. (2016, 2019) for Mg/Ni layer silicates of the serpentine (Srp) and talc (Tlc) groups from New Caledonia.

Figure 6: XRD patterns of oriented clay preparation of the five samples submitted to Ca saturation (a) and Li saturation (b) in the air-dried (AD) and ethylene glycol solvated (EG) states. Plain line CaAD or LiAD, dashed line: CaEG or LiEG. (b) two additional XRD pattern per sample: dotted line: Li_{300} after heating at 300°C (Hofman Klemen treatment), dash-dotted line: Li_{300}EG after heating at 300°C and solvation with EG.

723

724 **Figure 7:** Decomposition of XRD patterns of Li saturated clay fractions in AD and EG states
725 of the three most expandable samples (MG3aWill, BONBR2a and BONBR2c) in the angular
726 domain 3-13° 2 θ after background stripping. Dots: experimental values, plain lines: best fit,
727 dashed lines: elementary Gaussian contributions (in the EG state the Gaussian contribution is
728 identical with the best fit).

729

730 **Figure 8:** Position of the reflection at low angle (P1: 4-7 °2 θ) and at high angle (P2: 7-10
731 °2 θ) of the 2:1 component in CaEG and LiEG states, determined by XRD decomposition of
732 most swelling samples (MG3aWill, BONBR2a and BONBR2c).

733

734 **Figure 9:** XRD patterns of oriented preparation of the five clay samples saturated with K at
735 room temperature (AD 20°C, plain line) and after heating at 150°C (dashed line), 350°C
736 (dotted line) and 550°C (dash-dotted line).

737

738 **Figure 10:** Structure of the three components (a-TL, b-partly expanded stevensite and c-fully
739 expanded stevensite) of the interstratified 2:1 layer silicates. The increase of the d-spacing
740 from left to right is closely linked to an increase of vacant sites in the octahedral sheets and
741 hydrated cations (Mg, Ni) in the interlayer spaces.

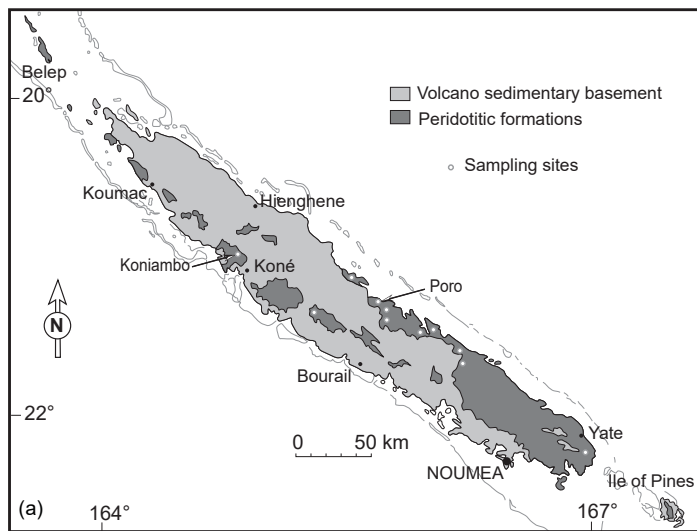


Figure 1

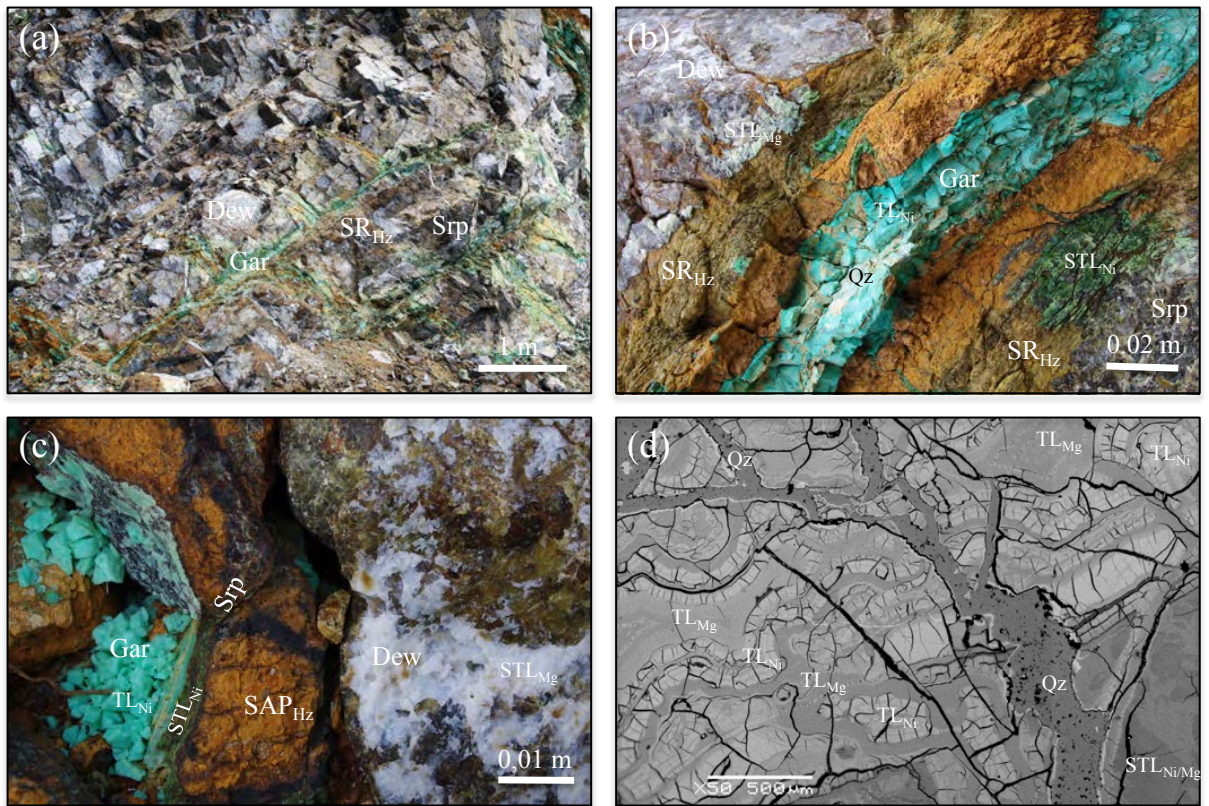


Figure 2

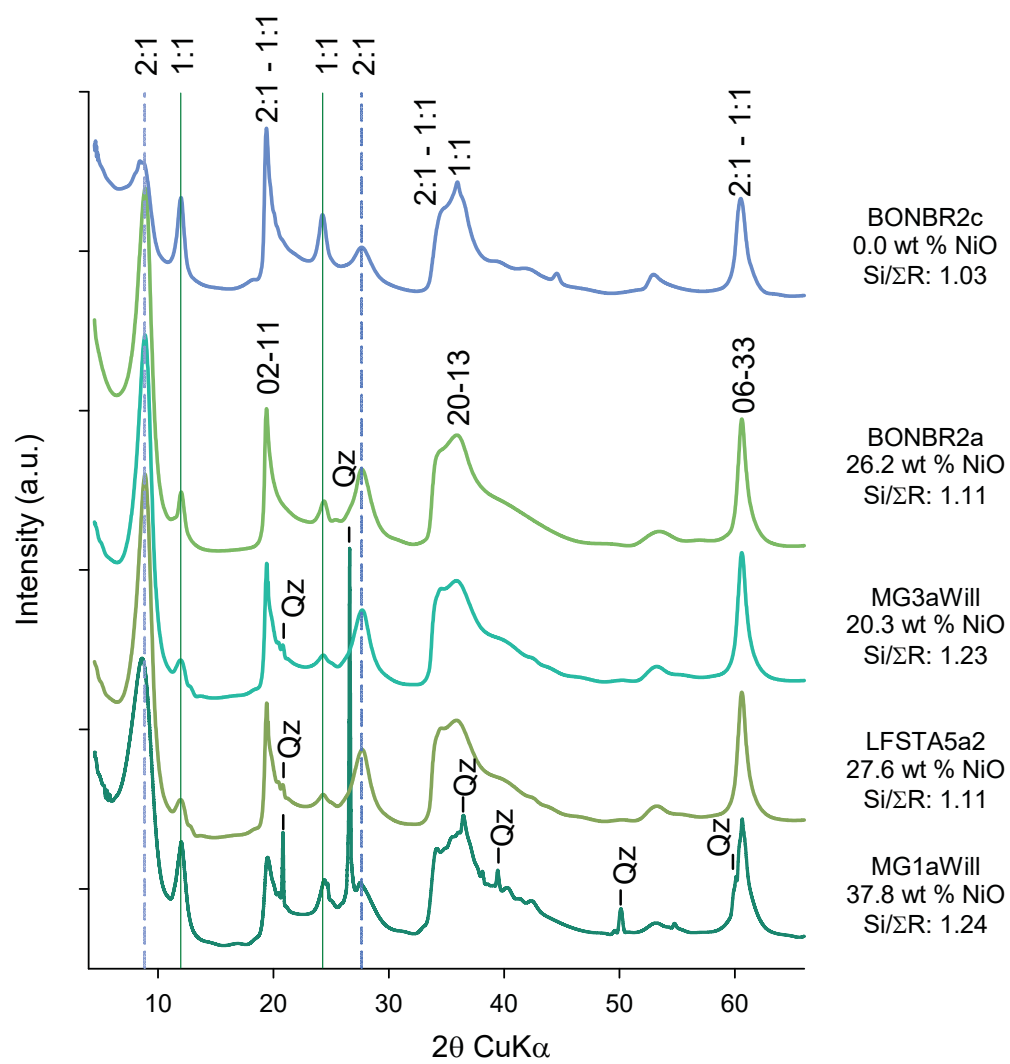


Figure 3

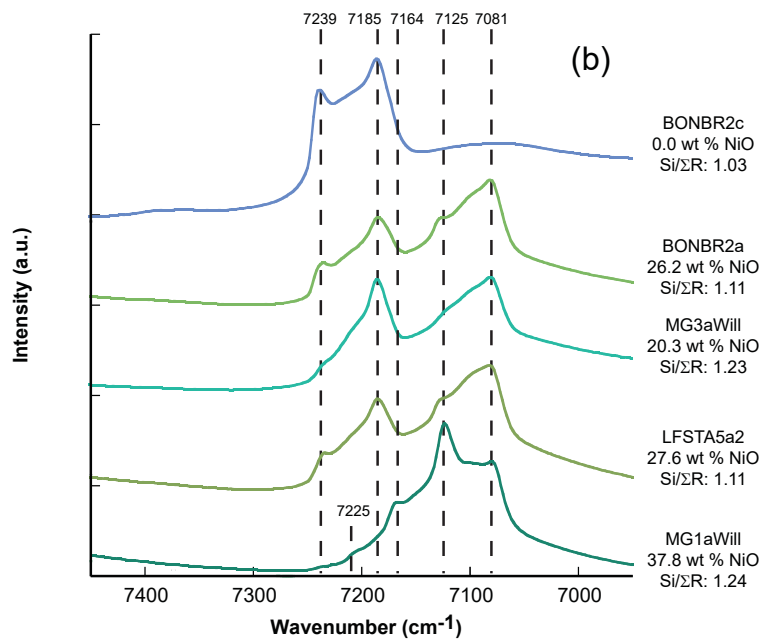
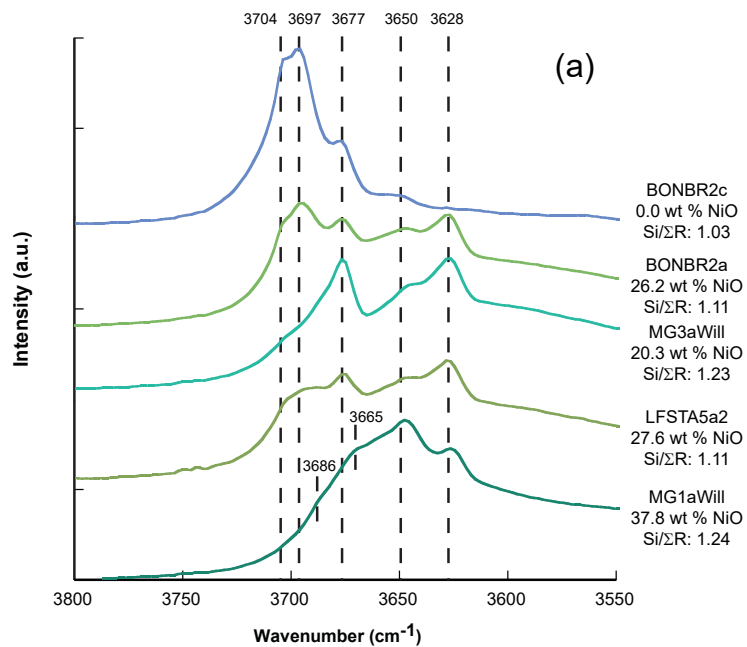


Figure 4

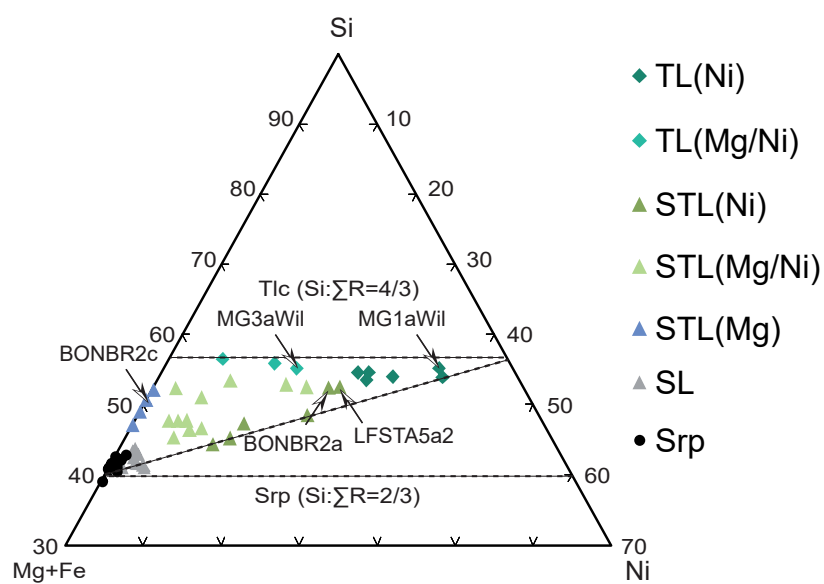


Figure 5

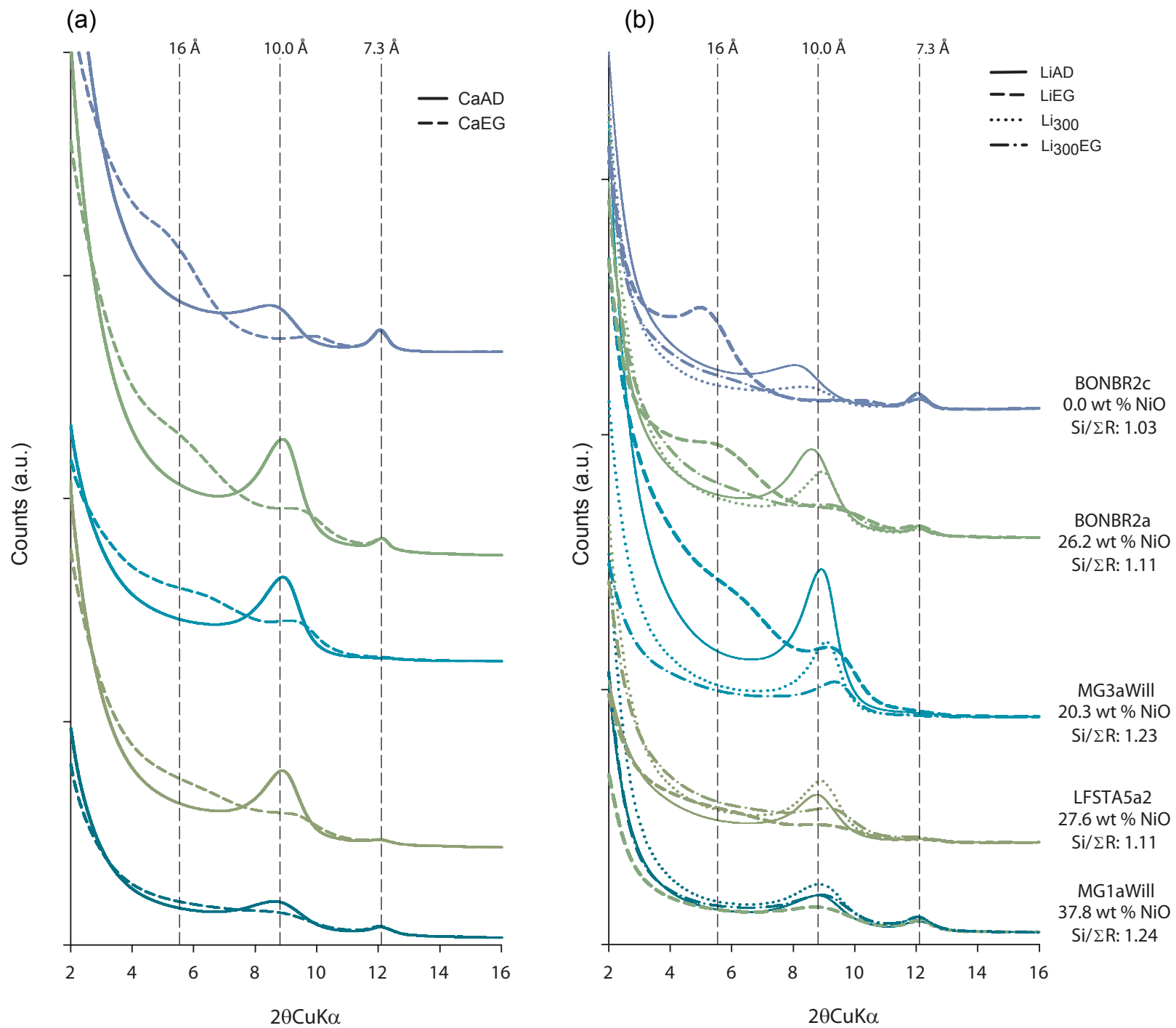


Figure 6

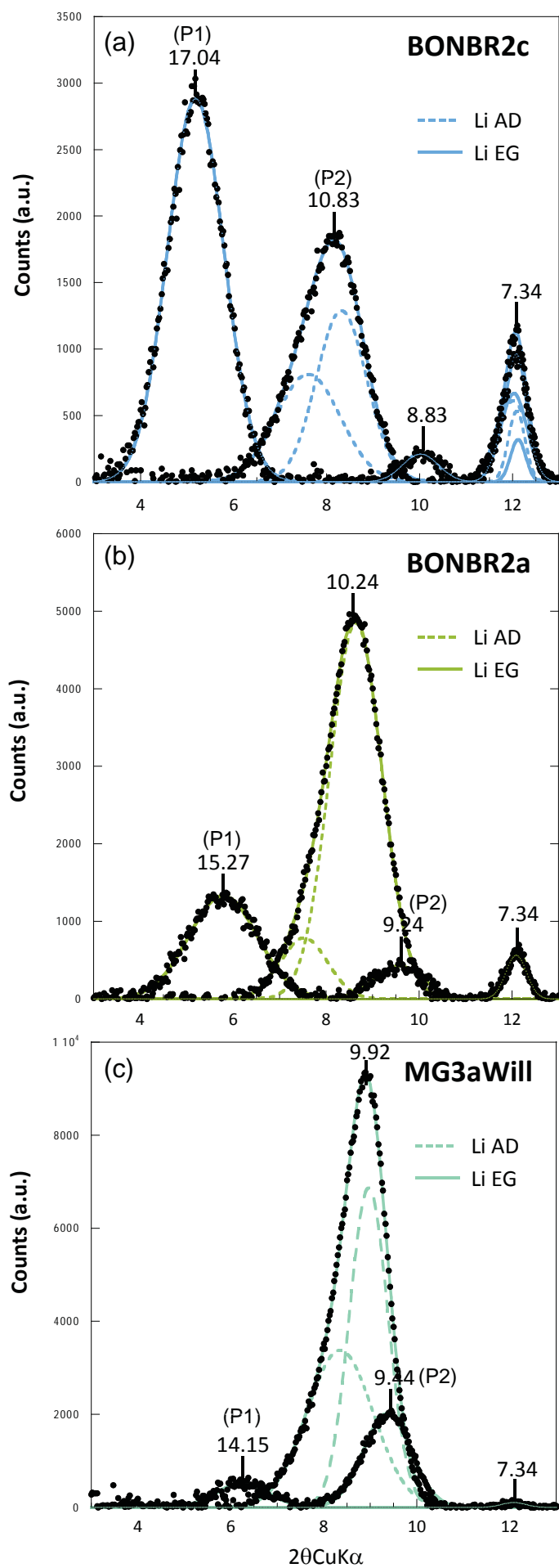


Figure 7

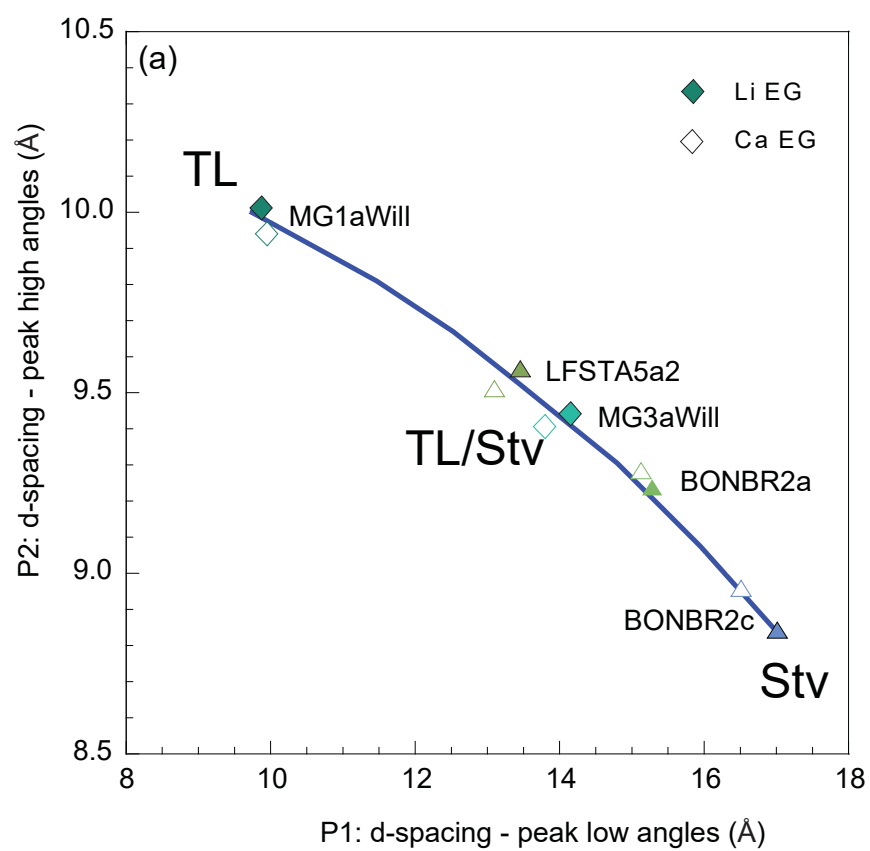


Figure 8

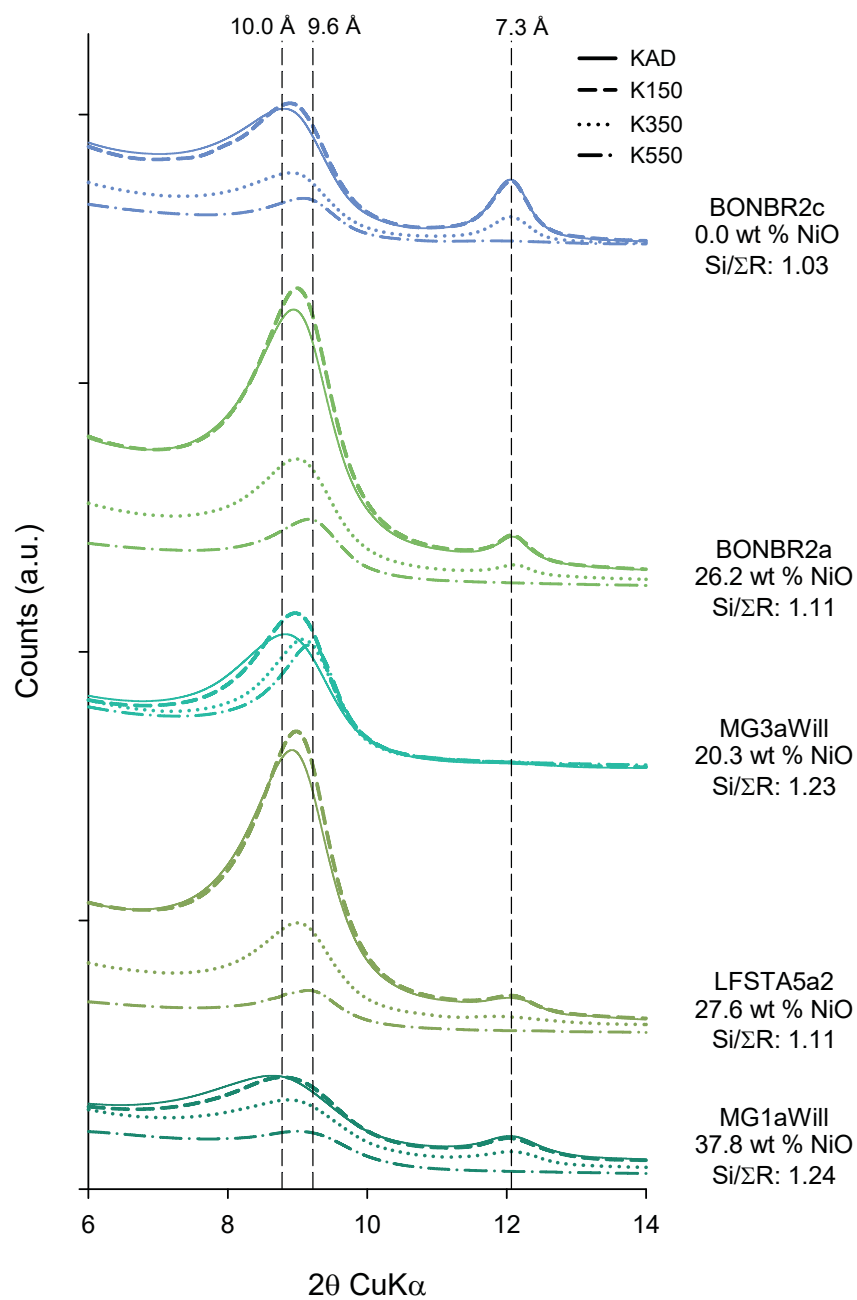


Figure 9

