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Combined XRF, XRD, SEM-EDS and Raman analyses on serpentized harzburgite (Nickel laterite mine, New Caledonia): implications for exploration and geometallurgy

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Supplementary information

Quantitative phase analysis by XRD

Olivine group: forsterite. The Rietveld refinement was not possible with the pure forsterite or Fe-Mg olivine but with the Ni substitution in forsterite.

The average nickel content in forsterite in our study is about 3000 ppm.

Results from a representative structure refinement of forsterite are shown in Table S1.

Table S1. Refined atomic parameters for forsterite

Atom	Wyckoff position	x/a	y/b	z/c
Mg1-Ni	$4a$	0	0	0
Mg2-Ni	$4c$	0.991	0.277	0.250
Si	$4c$	0.426	0.094	0.250
O1	$4c$	0.765	0.091	0.250
O2	$4c$	0.221	0.447	0.250
O3	$4d$	0.277	0.163	0.033

The refined unit-cell parameters of Ni-forsterite are $a = 4.74 \pm 0,01 \text{ \AA}$, $b = 10.19 \pm 0,01 \text{ \AA}$ and $c = 5.93 \pm 0,02 \text{ \AA}$, while those expected for pure forsterite are $a = 4.75$, $b = 10.20$ and $c = 5.98 \text{ \AA}$ ⁷⁸, proving the decrease of cell parameters. Since the \vec{c} axis is parallel to the edge-sharing M1-M1-M1 spine of the zigzag octahedral chain, a change in the M1 octahedron size has a

significant influence on the \vec{c} axis². The shrinkage of a is smaller because every second octahedral chain in this direction is unoccupied⁷⁹.

Table 2 indicates a strong preference of Ni^{2+} for the M1 site. Indeed, the occupancies are (in %): 98.1Mg + 1.9Ni in the M1 sites and 99.7Mg + 0.3Ni in the M2 sites. The M2 sites are larger than the M1 sites in forsterite. This implies that the larger cations Mg over Ni tend to occupy the larger M2 sites in olivine.

Pyroxene group: enstatite. The detected pyroxene in our XRD pattern is the ortho-enstatite with 11.6 ± 0.5 % of the total weight. Rietveld refinement analysis was performed then with orthorhombic enstatite based on the space group Pbca for texture correction.

The refined unit cell parameters are $a=18.318$, $b=8.853$ and $c=5.179$ Å with a crystallite size of 914 nm. The cell parameters values correspond to those reported in literature⁸⁰, for Ni-free enstatite.

Clay minerals: talc and sepiolite.

We encountered some problems to refine the talc phase and especially due to the shift of the peaks towards low angles compared to the expected values for Ni-free phase. This shift is due to the Ni substitution in Mg-talc⁸¹.

Rietveld refinement was possible with Ni-talc within the monoclinic space group C12/c1 using a simple isotropic crystallite size and microstrain line-broadening model.

The refined unit cell parameters are $a=5.421$, $b=9.158$, $c=18.283$ Å and $\beta=108.61^\circ$, with a crystallite size of 104 nm. The cell parameter values are smaller than those reported in the literature⁸². This suggests Ni incorporation in the talc structure. Indeed, as for forsterite, Ni substitution in the talc structure will induce a small decrease in the cell parameters compared to those of Ni-free talc.

For this phase, also (Table 2), a strong preference of Ni²⁺ for the M1 site is observed. Indeed, the occupancies are (in %): 78.1Mg + 21.9Ni in the M1 sites and 96.4Mg + 3.6Ni in the M2 sites, signing a much larger Ni incorporation in this phase, however less present in the sample.

Sepiolite $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, a soft white clay mineral, is detected in our XRD pattern with a weight fraction of 5.6 vol.%. For the refinement, we used the Ni-free sepiolite model proposed by Post et al.,⁸³. Within this model, sepiolite is orthorhombic, with the space group Pncn and approximate cell parameters $a = 13.422$, $b = 2a$, $c = 5.230 \text{ \AA}$ with a crystallite size of 115 nm. In the refinement, the occupation number of the different atomic positions corresponds to those given by Brauner and Preisinger⁸⁴, three hydrous species: OH anions in the O2 site, coordinated to Mg1, Mg2, and Mg3; structural H_2O at the O10 site, where it completes the Mg4 coordination at the edges of the Mg-(O, OH, H_2O) octahedral strips; and three zeolitic H_2O positions in the tunnels.

Quartz and periclase. α -quartz and periclase were also detected and refined. The presence of quartz (SiO_2) is related to serpentinization producing high amounts of silica in aqueous solutions. The quartz model (trigonal space group P3₂21) optimized in our study resulted in lattice parameters of $a = 4.920 \text{ \AA}$ and $c = 5.042 \text{ \AA}$ with a crystallite size of 250 nm. These latter are usual for quartz^{85,86}, observed here at 2.4%. For the refinement of periclase phase

(MgO, cubic, $Fm\bar{3}m$), a lattice parameter $a=4.209 \text{ \AA}$ is refined with a crystallite size of 132 nm. Periclase and quartz represent a sum of 6.2 % of the total volume.

Raman experiments

Serpentine group: lizardite. The modes at 130, 201, 231, 348, 388, 620, and 692 cm^{-1} are characteristics of lizardite serpentine. The strong band at 231 cm^{-1} is attributed to O–H–O vibrations, where O is the non-bridging oxygen of a SiO_4 tetrahedron and H is the hydrogen of the outer OH group of the adjacent layer¹⁰. The band at 130 cm^{-1} is attributed to the Si–Ob–Si bending mode³³. The weak bands at 201 and 348 cm^{-1} are assigned to the A_{1g} mode of $\text{Mg}(\text{O},\text{OH})_6$ group and to the SiO_4 bending mode, respectively³². The large band at 462 cm^{-1} is associated to the deformation of the $\text{SiO}_4\text{--MgO}_4$ tetrahedra¹¹. The intense band at 691 cm^{-1} is attributed to the symmetric stretching mode (ν_s) of the Si–Ob–Si groups¹¹. The band at 388 is observed in the spectra and assigned to the $\nu_5(e)$ bending modes of the SiO_4 tetrahedra^{30,31}. The band at 620 cm^{-1} is assigned to OH–Mg–OH translation modes.

Olivine group: forsterite. Olivine has 81 optical modes but only 36 of which are Raman active ($11A_g + 11 B_{1g} + 7B_{2g} + 7B_{3g}$)^{35,36}. For forsterite, the Raman spectrum (Figure 6b) can be divided into 3 regions: $<400\text{ cm}^{-1}$, $400\text{--}800\text{ cm}^{-1}$ and $800\text{--}1100\text{ cm}^{-1}$. Bands between 800 and 1000 cm^{-1} can be classified as internal stretching vibrational mode of SiO_4 tetrahedra. The dominant feature in this region is a doublet with peaks at 821 and 852 cm^{-1} . These peaks result from coupled ν_1 symmetric and ν_3 asymmetric vibrations of SiO_4 tetrahedra^{35,40}. Bands in the $400\text{--}800\text{ cm}^{-1}$ region are mainly from SiO_4 internal bending vibrational modes, while those below 400 cm^{-1} are dominated by the rotation and translation of the tetrahedra $(\text{SiO}_4)^{4-}$ as well as magnesium motion³⁵.

3.3. Raman experiments.

Pyroxene group: enstatite. Raman vibrational modes were observed for enstatite in the wavenumber range between 100 and 1200 cm^{-1} . Raman spectrum of enstatite (Figure 6c) is characterized by (1) the stretching Si-O non-bridging and bridging modes at $1015 \pm 20\text{ cm}^{-1}$ and $870 \pm 50\text{ cm}^{-1}$,

respectively; (2) the symmetric Si-O-Si bending modes at $670 \pm 20 \text{ cm}^{-1}$ and (3) metal-oxygen bending and stretching modes below 600 cm^{-1} .^{41,87}

Reynard et al.,⁷⁸ reported a quick way to identify enstatite polymorphs using Raman spectra. There is a cell doubling in going from protoenstatite to orthoenstatite and correspondingly more peaks are observed in the Raman spectra of orthoenstatite compared to protoenstatite. Indeed, a single peak around 675 cm^{-1} can be used as diagnostic feature for protoenstatite, whereas orthoenstatite exhibits a doublet in the same frequency region (665 and 690 cm^{-1}). Therefore, the lower spectrum can be assigned as orthoenstatite. This finding is in agreement with stability field of orthoenstatite in peridotite rocks, while the clino to protoenstatite transformation occurs at temperature at about 1250°C ⁸⁸.

Clay minerals: talc.

The spectrum has two strong Raman bands around 193 cm^{-1} and 674 cm^{-1} . The later band is attributed to symmetrical stretching vibrations of the Si\O(bridging)\Si bond in SiO_4 tetrahedra, while the former at 193 cm^{-1} can be attributed to the stretching vibration of MO_6 octahedra (where M is Mg and/or

Ni) of a talc-type structure^{44,45}. The weak Raman bands at 1053 and 1023 cm⁻¹ are assigned to $\nu_4(e)$ and $\nu_2(e)$ non-bridging Si-O stretching modes, respectively. Raman spectrum shows the expected $\nu_6(e)$ and $\nu_3(e)$ modes of SiO₄ at 458 cm⁻¹ and 410 cm⁻¹, respectively. In addition, a relatively intense band at 364 cm⁻¹ attributed to $\nu_5(e)$ modes of SiO₄ are present in the spectrum. For Mg-talc, the stretching vibration of MO₆ octahedron band of talc is expected at 196 cm⁻¹.

Table S2. Raman vibration modes of lizardite, forsterite, orthoenstatite and Ni-talc. The symmetries and assignments are based on those reported in literature

Symmetries and assignments	Raman shift (cm ⁻¹)
Lizardite ³⁰⁻³³	
Si-Ob-Si bending mode	130
A _{1g} mode of Mg(O,OH) ₆ group	201
O-H-O vibrations	231
A _{1g} mode of Mg(O,OH) ₆ group	348
$\nu_5(e)$ bending modes of the SiO ₄ tetrahedra	388
SiO ₄ -MgO ₄ tetrahedra	462
OH-Mg-OH translation modes	620
(ν_s) of the Si-Ob-Si groups	691

Forsterite ^{35,36,40} Internal stretching vibrational mode of SiO ₄ tetrahedra SiO ₄ internal bending vibrational modes Rotation and translation of (SiO ₄) ⁴⁻ and magnesium motion	< 400 400-800 800-1100
Orthoenstatite ^{41,87,88} Metal-oxygen bending and stretching modes Symmetric Si-O-Si bending modes Si-Ob-Si bending mode Si-O non-bridging mode	< 600 670 870 1015
Ni-Talc ^{44,45} Stretching vibration of MO ₆ octahedra MO ₆ octahedron band ν ₅ (e) non-bridging Si-O stretching modes ν ₃ (e) non-bridging Si-O stretching modes ν ₆ (e) non-bridging Si-O stretching modes Si\O(bridging)\Si bond ν ₄ (e) non-bridging Si-O stretching modes ν ₂ (e) non-bridging Si-O stretching modes	193 196 364 410 458 674 1053 1023

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