ALTERATION OF ASBESTIFORM MINERALS UNDER SUB-TROPICAL CLIMATE: MINERALOGICAL MONITORING AND GEOCHEMISTRY. THE EXAMPLE OF NEW CALEDONIA

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INTRODUCTION

The rising awareness in risk due to asbestos environmental exposition leads to a new interest in the *in situ* identification of mineral fibres. *Asbestos* is the commercial and regulatory designation for a group of six-silicate mineral fibres of the serpentine (chrysotile) and amphibole (amosite, crocidolite, anthophyllite, tremolite, actinolite) groups (IARC, 2012; EU, 2003). Because of their peculiar physical-chemical (*e.g.*, crystal habit, flexibility) and technological proprieties (*e.g.*, heat resistance; Williams *et al.*, 2013) asbestos has been exploited by industry since the second half of 19^{th} century. Actually, asbestos mineral fibres are present in natural environment (rocks and soils) as a result of geological processes. Naturally Occurring Asbestos (NOA) includes deposits resulting from widespread use of asbestos-containing products, rather than to natural deposits that have been exposed unintentionally by excavation, road grinding, or mining. In this context, weathering and human activity may disturb NOA-bearing rocks (or soils) and release mineral fibres into the air.

The investigation of NOA started after the diagnosis of asbestos related pathologies in human populations non-occupationally exposed to asbestos (Luce *et al.*, 2004; Gunter *et al.*, 2007a, 2007b; Culley *et al.*, 2010; Thompson *et al.*, 2011; Bayram *et al.*, 2013). In environmental contexts, inhalation is due to a large diversity of fibres whose impact on the health is potentially much greater than the six-regulated asbestos minerals (IARC, 2012). Other asbestiform fibres have been shown to cause chronical diseases (*e.g.*, fluoro-edenite asbestos and erionite; IARC, 2012) or to be potentially toxic to human (*e.g.*, balangeroite; Gazzano *et al.*, 2005; Groppo *et al.*, 2005; Turci *et al.*, 2005). Moreover, the lack of comprehensive scientific data on toxicology of non-regulated fibrous minerals helps to understand difficulties in assessing the potential risk due to environmental exposition.

In humid tropical to sub-tropical climate conditions, NOA-deposits shall be subjected to a further process of alteration as a result of weathering processes. With the term *alteration* we refer to a physical-mechanical modification in the appearance and/or shape of amphibole and serpentine mineral habits. Increasing the degree of alteration, massive assemblages gradually cleave into lamina or needle-like acicular crystals. This progressively loss of cohesion leads to the disappearance of the original structure, and conversely to the appearance of individual asbestiform fibres at the surface. Minerals which have been subjected to supergene alteration may thus vary from prismatic-platy through acicular-lamellar to asbestiform. Because of the wide range of natural shapes, morphologies, and alteration status occurring in mineral fibres impacted by weathering, it seems very difficult to discriminate these fibres. NOA is a complex task which involves different analytical approaches depending on the characteristic of the sample (rock, bulk, filter) and, more important, on the purpose of assessment (Nichols *et al.*, 2002; Cavariani *et al.*, 2010). The principal methods listed in the distinct norms and used by commercial-asbestos laboratories to identify asbestos have therefore to be applied to natural samples. In this context, the New Caledonia proved to be a good example for the investigation of impact of supergene alteration in the genesis and release of fibres into the environment. The huge variety of asbestiform minerals and their distribution over a large part of the Grande Terre Island make environmental asbestos a major public health issue for New Caledonia.

ASBESTOS HEALTH HAZARDS IN NEW CALEDONIA

The natural occurrence of fibrous minerals in New Caledonia has been reported more than 20 years ago (INSERM U88, 1997). Covered by ultrabasic units for more than a third of its surface, the New Caledonia (South West Pacific) is one of the largest world producers of Ni-ore from lateritic deposits. According to the current understanding, the Boghen terrane in the central unit, the ultrabasic complex related to mining context, and the northern metamorphic complex of the Grande Terre Island, are the three geological units most impacted by the presence of asbestiform mineral fibres (Fig. 1; Lahondère, 2007, 2012; DIMENC-SGNC, 2010). While (fibrous-asbestiform) tremolite is mainly present in central and northern New Caledonia terranes, serpentine chrysotile and fibrous-lamellar antigorite occur in peridotites. Moreover, as a consequence of supergene alteration, Caledonian specimens show a very altered appearance, characterized by a structureless and friable aspect, compared to most of the natural worldwide asbestos occurrences (*e.g.*, Western Alps, Haute-Corse; ANSES, 2010).

Caledonian populations, living and/or working on proximity of natural outcrops, are therefore subjected to a double environmental and domestic exposure to asbestos and related mineral fibres. Meanwhile, recent statistical and epidemiological data correlated the high mesothelioma incidence of Caledonian population to the presence of chrysotile and fibrous-lamellar antigorite on the outcrops, in tracks and soils (Lahondère, 2007; Baumann *et al.*, 2011).

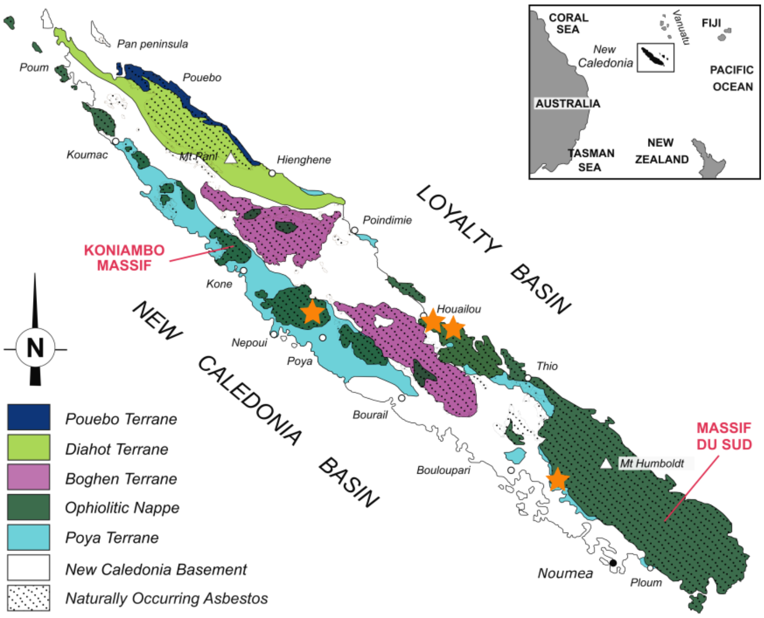

Fig. 1 - Geological sketch map of New Caledonia (modified after Cluzel *et al.*, 2001). Potentially NOA are reported (DIMENC-SGNC, 2010). Sampling sites are indicated with star.

In the restriction of risk due to fibre exposition, the New Caledonia legislation (*Déliberation N°82 du 25 Aout 2010*) introduced serpentine-antigorite in the list of regulated-asbestos. This directive is the first in the world to include a new fibrous mineral in regulations. Actually no conclusive data on fibrous-antigorite toxicity are available (ANSES, 2014). However, from a morphological point of view, recent studies confirm the fibrous-lamellar nature of Caledonian antigorite (Laporte-Magoni *et al.*, 2018).

Mining companies developed a monitoring prevention plan based on a preliminary on-field identification, followed by an analytical investigation (NF X43-269). However, to date, no accredited laboratory are available locally. Time-consuming analysis is too long when compared to mining and professional timelines. In this context, the establishment of an effective *in situ* diagnostic strategy is a requirement.

THE RESEARCH PROJECT

This research project aimed to improve the current procedure envisaged by mining geologists for the mineral identification on-field, and to evaluate the impact of supergene alteration on the recognition of asbestos and on fibres genesis. A diagnostic routinely analytical strategy, able to discriminate and characterize the different varieties of the asbestiform phases *in situ*, directly on the natural outcrop, under normal environmental conditions (sun, strong wind, high temperature, etc.) was developed. Because of the altered appearance of Caledonian rock-fragments, a complete mineralogical approach was performed to characterize these mineral fibres. An exhaustive sampling of the different types (mineralogy and alteration status) of mineral fibres naturally occurring in mine context (outcrops, quarries, tracks, pit) of different geological units was carried out. Studied samples include serpentine minerals such as chrysotile, and fibrous antigorite, as well as tremolite-amphibole. Data obtained with the more traditional mineralogical and petrological techniques – such as polarized light microscopy (PLM), X-ray powder diffraction (XRPD), scanning electron microscopy (SEM-EDS), and transmission electron microscopy (TEM-EDS) – have been completed by the employment of more specialized tools as polarized light microscopy coupled with a dispersion staining method (PLM/DS) and micro-Raman spectroscopy. A portable/handheld Raman equipment was test under different climate conditions, even in presence of strong altered samples. Additionally, a preliminary study of the potential presence of asbestos in the lateritic soils (soft yellow and red limonite soils) was performed.

It should be remembered that supergene alteration is a multi-factors process. Chemical processes at the rock/fluid interface play an important role in the supergene alteration processes. The circulation of water is one of the main strong agent in chemical weathering. Thus, the most soluble elements may be leached by water, leading to the dissociation of fibrous minerals and consequently favouring the emission of fibres. The study of major and trace element concentrations may therefore represent a tracer of the impact of weathering on altered rocks. A preliminary geochemical investigation has been approached. A detailed study of chemical composition of mineral fibres at increasing degree of alteration was carried out by ICP-OES and ICP-MS spectrometry. Moreover, two batch-leaching experiments, aimed to simulate the weathering processes under a controlled environment, were realized to evaluate the influence of physical-chemical parameters (*e.g.*, pH, temperature, *etc.*) on chemical alteration of rock fragments. Study focused on the estimation of the role of chemical element exchange on the capacity of dispersion of fibres. The first experiment aimed to reproduce experimentally the rainwater action (MES buffered solution, 0.01 M, pH = 5.6) on apparently non-altered samples (minimum degree of alteration). During the second experiment a chelating chemical agent (DTPA buffered solution, 0.005M, pH = 7.3) was used to force extraction. The objective was to observe the behaviour of samples under extreme conditions of extraction. Finally, the role of leaching processes in the physical-mechanical dissociation of rock fragments into fibres was evaluated.

RESULTS AND DISCUSSIONS

Mineralogical investigation of mineral fibres and environmental monitoring

Caledonian samples have a wide and more complex mineralogical nature than expected. Data achieved describe a complex situation, whereby each instrumental device implies advantages and limits. This means that a multidisciplinary routinely approach is the only strategy possible to answer to worker and population requirements.

PLM is a preliminary essential technique in the study of textures and mineralogical associations. It has proved to be a valuable tool in the investigation of morphologies but, unfortunately, it cannot be suitable for monitoring operations. Although the 2-dimensional nature of petrographic thin sections makes difficult to distinguish the crystal habit (*e.g.*, fibrous, acicular, and lamellar), PLM observations allowed to evaluate the finely intergrowth of different fibrous or non-fibrous

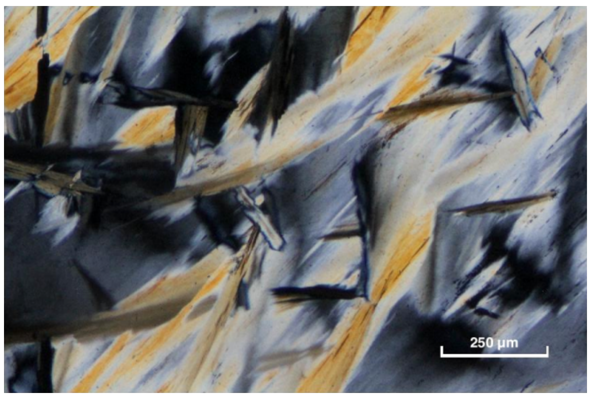

Fig. 2 - PLM cross-polarizing image showing an unusual and potential new type of texture, characterized by star and fan formed aggregates. Finely intergrowth of fibrous antigorite and chrysotile fibres at the micro-scale.

phases in their textural context, revealing also the presence of potential new type of texture (Fig. 2). Samples that appeared massive, lamellar, non-altered in the hand sample might display their fibrous shape already at the PLM scale.

SEM is a powerful technique that enables to determine the quantitative (size and distribution), morphological, and semi-quantitative composition (EDS system) of asbestos fibres. Compared to literature where most of morphological images have been acquired at 10-20 kV, with the intent to better evaluate the general morphology of fibres, we chose to work at lower voltage (5-10 kV), in order to focus attention on the study of surface features. SEM images, acquired especially in SEI (Secondary Electron Imaging) mode, provided to be the best way for the description of the huge morphological variability exhibited by mineral fibres of New Caledonia. Caledonian chrysotile, for example, is characterized by a massive compact appearance. Contrary to what expected in published literature (*e.g.*, Andreani *et al.*, 2004), it is formed by the close overlapping of thin fibrils, resulting in a high density of tubes (Fig. 3). Furthermore, the appearance of several individual fibres at the surface was observed for all samples.

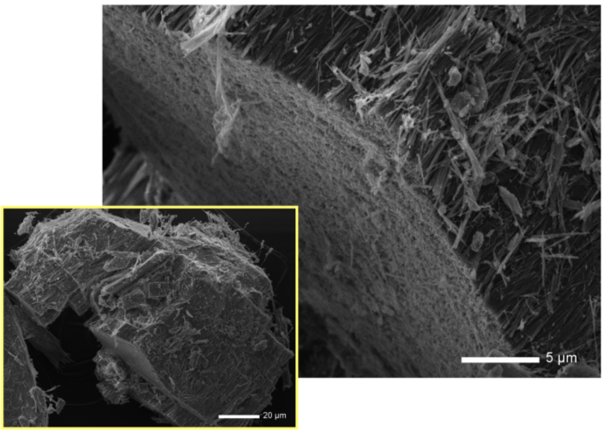

Fig. 3 - SEM images of compact bundle of parallel fibrils of chrysotile.

TEM is the most complete method in the characterization of small particles, combining morphological information (TEM imaging) to chemical data (EDS system) and crystallographic characterization (SAED). Only at TEM-scale magnification it is possible to observe certain structural details, such as an unusual enlargement of internal nanotube of chrysotile and/or several intimate mineral associations at the sub-microscale. In this study TEM microscopy was applied only to samples which have proved to be more difficult in interpretation.

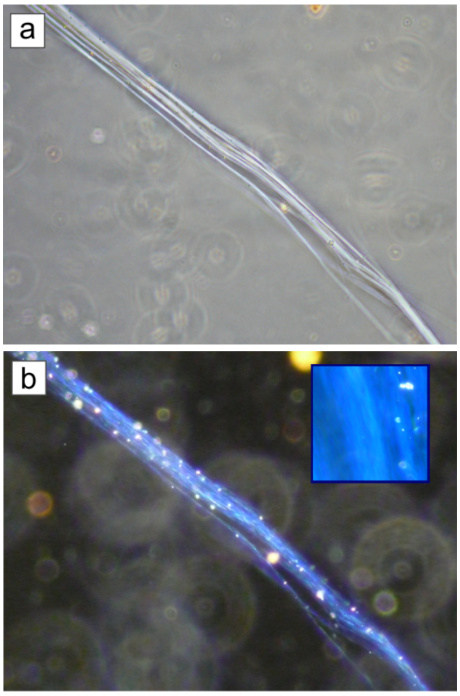

Fig. 4 - Identification of fibrous-antigorite by PLM/DS, RI 1.5680. In Phase Contrast observation fibres show a pale-blue to white colour, without halo (a), whereas they are amazing in blue indigo colour in Dark Field observation (b).

PLM/DS observations on mount particles allowed to successfully identify all fibrous samples analysed, providing information about mineralogical identification and morphology of fibres and/or lamellae. The implementation of Refractive Index (RI) 1.5680 liquid in regulated protocols would allow to discriminate antigorite from chrysotile fibres (RI 1.550; Health and Safety Executive, 2006). Because of the lack of guidelines provided by regulations for the discrimination of non-asbestos serpentine minerals, a specific work aimed to find the RI liquid that match most closely the RI value of antigorite was realized. The RI 1.5680 has provided to be the RI liquid that mostly matches the antigorite phase, showing characteristic dispersive colours, as clearly shown in Fig. 4. Repeating in routine this simply and rapid technique on several particles for each sample, PLM/DS may be an efficient tool in characterization of asbestos in rock samples. By contrast, its main limit is essentially related to detection of thin smaller particles. While PLM/DS allows to investigate different population of particles in the range of micrometre scale (10-300 µm), electron microscopies techniques give information until nanometric scale (TEM resolution, 0.01-10 µm; Cavariani *et al.*, 2010).

X-ray powder diffraction was performed on all samples for the qualitative determination of the main crystalline components. As expected, XRPD may be used as quick, user-friendly technique only in the qualitative recognition between amphibole and serpentine minerals. On the contrary, due to the low sensitivity in the distinction of the different varieties of serpentine group, XRPD cannot be involved in a routinely monitoring systems. The information conveyed by simple X-Ray qualitative analysis is not sufficient to handle the complexity of these mineral structures and assemblages (Foresti *et al.*, 2003; Gualtieri *et al.*, 2014).

The acquisition of Raman spectra in low-wavenumber region and OH-stretching region (high-wavenumbers) was confirmed as the decisive approach for the identification of the main varieties of the serpentine and amphibole families. OH is a very sensitive probe for the micro-structure investigation of asbestos minerals, allowing the discrimination of intimately intergrowth of fibrous minerals at the microscale (Petriglieri *et al.*, 2015). In order to test the performances of portable Raman equipment, a set of preliminary measurements was performed in laboratory. A test for each sample (one or two spot analysis at most) was performed. On 47 analysed samples, 41 were successfully identified, allowing the discrimination of the main serpentine or amphibole phase. A comparison of spectra obtained with micro-Raman spectrometer (laboratory device) and portable Raman (handheld equipment) on a chrysotile sample is shown in Fig. 5. The micro-Raman spectrum was recorded on petrographic thin section, on a polished surface, choosing the optimal conditions of measurement.

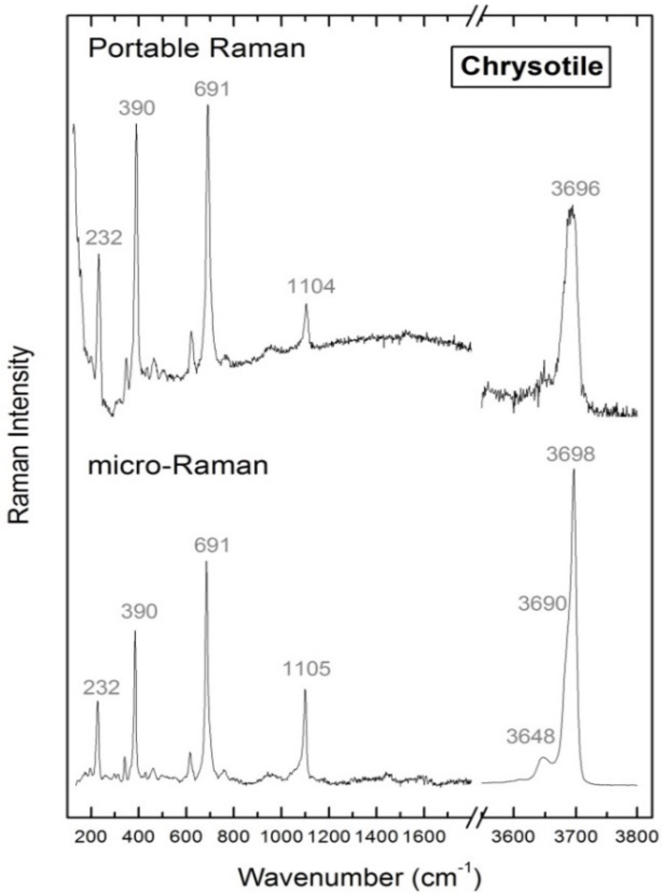

Fig. 5 - Comparison of spectra recorded with a micro-Raman spectrometer (473.1 nm laser) and a portable Raman device (532 nm laser).

On the contrary, the portable Raman does not allow the choice of all these instrumental parameters. In this latter case, the acquisition was performed directly on fibre bundles, selecting only the time of acquisition. Moreover, differences in spatial (1-2 µm and 1 mm, respectively) and spectral (4 cm^{-1} and 8 cm^{-1}, respectively) resolution shall be taken into account. In addition, the quality of the signal-to-noise ratio, and consequently the quality of the spectra, may be affected by the fluorescence interference. Despite all these intrinsic differences, spectra appear perfectly comparable at both low- and high-wavenumber regions, allowing the identification of the mineral phase.

Alteration of asbestos, element release and fibre emission

A physical-mechanical stress is probably the main reason for alteration status associated to mineral fibres dissociation. Using the example of serpentine minerals, SEM images show that for both "less contaminated" (*i.e.,* only antigorite) and mixed (*i.e.* antigorite + chrysotile) samples, we observed an increase of porosity as the degree of alteration increases. A gradual increase of distance between closely overlapped fibres and/or fibrous-lamellae was observed. This is probably related to the circulation of water, flowing preferentially into cracks, fractures and weakness areas. Thus, the penetration of fluids within fibrils is favoured and causes a stronger mechanical stress, until the completely loss of cohesion of the original structure. Furthermore, the great variability of morphologies displayed by Caledonian samples and the increasing degree of alteration are not necessarily correlated.

On the other hand, weathering does not cause modification in the crystallographic structure of the asbestos varieties. Comparing the XRPD patterns at increasing degree of alteration, they appear perfectly comparable: no differences occurred in peak positions (no shift), or even in peak broadening. Additionally, any neo-formed mineral phases associated to supergene alteration were recorded. Although the crystalline structure of fibres is not influenced by supergene alteration, there is a natural chemical exchange at the fibre/water interface, resulting in the release of elements.

As a result, the surface chemical compositions of fibres are modified. Analysis on major elements show a systematically lower Mg- and higher FeO_{tot}-content in all Caledonian antigorite samples, compared to MgO and FeO values displayed by worldwide serpentine-antigorite (from 35 to 45, and 2 to 5 wt.% respectively; Deschamps *et al.*, 2013; Critelli *et al.*, 2015; Cannaò *et al.*, 2016). Magnesium is known to be a solvable element during spring water circulation on serpentinite rocks. Thus, increasing the alteration of antigorite, an overall decrease of MgO concentration should be expected, as shown in Fig. 6. For these reasons, we can therefore assume that even apparently non-altered samples are characterized by an initial degree of alteration.

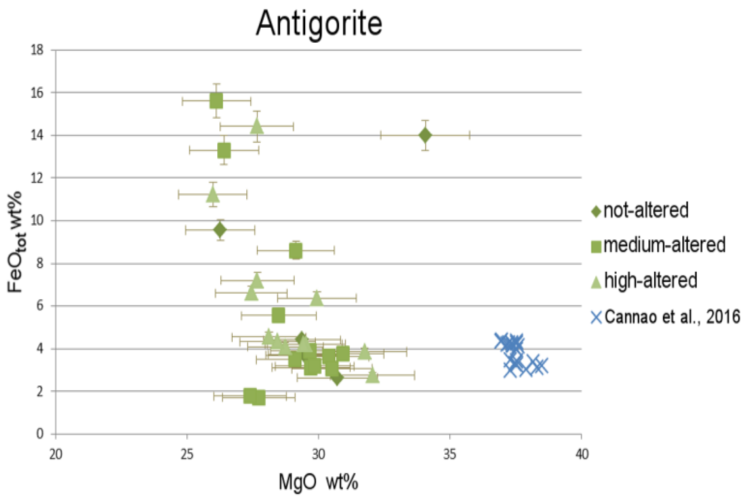

Fig. 6 - FeO_{tot} wt.% *vs.* MgO wt.% for antigorite. Concentrations of antigorite of the Voltri Massif (Alps, Italy) are reported for comparison (Cannaò *et al.*, 2016).

These results are consistent with SEM observation, exhibiting the appearance of individual thin, potentially breathable, fibres at the fragment surface. Furthermore, considering only the so-called "less contaminated" antigorites, the highest concentrations in FeO_{tot} occur in the samples associated to the high degree of alteration. This result is crucial in the study of the asbestiform nature of Caledonian samples. The toxicology of asbestos is strictly related to fibres morphology, but also to iron release in lung tissue (Fubini & Fenoglio, 2007).

After the batch-leaching experiments, an increase in Mg, Ca, Fe, Mn, Ni, Co, and Cr concentrations in the supernatant was recorded. As shown in Fig. 7, metal concentrations in the supernatant solution increase with time until a maximum value and, then, decrease.

Metal elements are therefore solubilized from mineral fragments and then precipitate if the solution is saturated (according to pH increase). Moreover, the analysis of the suspended particulate matter shows the presence of a mixture of fibres and non-fibrous particles, with a mainly abundance of fibres morphologies. It is worth noting that the amount (wt.%) of suspended particulate matter increases with time of extraction, especially when the extracting solution is DTPA.

Fibres emission is then undoubtedly due to the element solubilization. The physical-mechanical effect of fluid circulation within fibres and lamellae, associated to chemical elemental exchange at rock/waters interface favoured the dissociation of fibres and their release into the environment. The same approach will be applied to the investigation of chrysotile and tremolite.

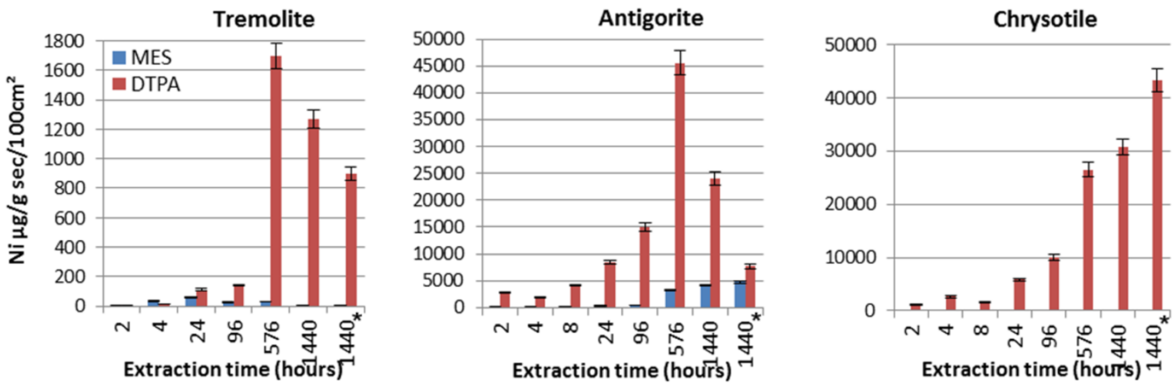

Fig. 7 - Ni concentration in the supernatant as a function of time for leaching experiments with two solutions MES and DTPA. * for experiments conducted with several asbestos-fragments leading possible mechanical effect on alteration during shaking.

Monitoring environmental risk in mining context

In order to test portable Raman equipment on field, directly at the mining front, under normal environmental conditions, two field trips at the open mines of Balangero (ex-asbestos chrysotile mine, Italy) and Tontouta (Ni-laterite ore, New Caledonia) were carried out. Portable Raman has proved to be a reliable user-friendly technique in the *in situ* identification of mineral fibres under both temperate and sub-tropical climate conditions.

Overall 67 spot were analysed: 80% were successfully identified allowing the identification of the typical mineralogical association. On the other hand, the implementation of another complementary analytical methodology, as for example PLM/DS, could be the answer for the discrimination of not-identified spot samples (the remaining 20%). Finally, to better evaluate the real risk for mining workers due to exposition to mineral dusts, a preliminary study on the potential presence of free fibres in contaminated laterite soils was carried out. Unfortunately, XRPD and SEM analysis confirm the presence of the asbestiform varieties of the serpentine family into the Ni-ore soils. Further analyses are required to better understand the real risk related to manipulation of these contaminated lateritic soils.

CONCLUDING REMARKS

In the environmental monitoring identification of mineral fibres, a multidisciplinary routinely approach, based on the use of complementary simply-to-use analytical methods is the only strategy possible. In addition, the instrumental apparatus has to be easily transportable on the field, directly on the mining site. The employment of specialized tools such as Polarized Light Microscopy associated to Dispersion Staining (PLM/DS) and portable Raman spectroscopy for identification of environmental asbestos are proved extremely effective in the improvement of the performance and rapidity of data acquisition and interpretation. Both PLM/DS and handheld Raman devices confirmed to be discriminant in the detection and characterization of asbestos fibres for both serpentine and amphibole. Furthermore, they resulted extremely effective even in the presence of strongly fibrous and altered samples, like the Caledonian ones. Tests realized in mining context, at the open pits of Balangero (Italy) and Tontouta (New Caledonia), have confirmed their high diagnostic power. In order to guarantee the optimal employment of both these devices, a training formation of the operators is required. Regardless of the alteration status of Caledonian specimens, geochemical analyses demonstrate how the physical-mechanical effect of fluid circulation within the porous of fibres and/or lamellae, associated to chemical elemental exchange at rock/waters interface, favoured the dissociation of fibres and their release into the environment. It is worth noting that all these considerations may applied to all type of unconfined sites of exposition, including environmental and domestic expositions.

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