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HIGH TEMPERATURE REACTIONS OF SERPENTINE GROUP MINERALS

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INTRODUCTION

The serpentine minerals lizardite, chrysotile, and antigorite are trioctahedral hydrous phillosilicates based on 1:1 layer structures with one tetrahedral and one octahedral sheet. The three serpentine minerals have similar chemical composition, with the occupancies of the octahedral sites dominated by magnesium.

The transformation of serpentine minerals to forsterite (or olivine) by heating in air has been extensively studied in the past with the main objectives to identify the products formed and the determination of the thermal changes accompanying the process. Their structural and mineralogical modifications under increasing P-T or deformation conditions have primary implications in subduction zones, fault dynamics, and seismic behaviour (*e.g.*, Ulmer & Trommsdorff, 1995; Escartin *et al.*, 2001; Peacock, 2001; Boudier *et al.*, 2009). Serpentine minerals and their behaviour at high temperature are receiving increasing attention as an expression of hydration in the mantle and the water cycle in the deep Earth. Serpentine, in fact, may develop from water penetrating the mantle by cracking in the brittle regime of the oceanic lithosphere at temperatures below 500-600 °C. Thermal behaviour of serpentine group minerals has been widely studied in the past, with major attention to chrysotile because of its obvious relevance to many high-temperature uses of asbestos fibres or composite materials containing such fibres.

Despite the huge amount of work devoted to the temperature-induced dehydroxylation and recrystallization reactions of serpentine minerals in air at ambient pressure, several issues are still open to debate or missing: *i)* the nature and stability of amorphous dehydroxylate phases, *ii)* the nature and stability field of talc- and chlorite-like phases possibly appearing during the reaction path, *iii)* possible topotactic relationships between the serpentine and the newly formed phases forsterite and enstatite, *iv)* the nature of the pyroxene phase, and *v)* a comprehensive model based on kinetic parameters.

The results of this PhD thesis provide information in order to confirm the nature and the stability of amorphous dehydroxylate phases, the nature and the stability field of talc-like phases, possibly appearing during the reaction path, and the possible topotactic relationships between the serpentine and the newly formed phases forsterite and enstatite.

The purpose of this PhD thesis was to study the high temperature reaction sequences of the serpentine minerals and to characterize the product of the thermal treatment of asbestos-cement, also in a view of a possible recycling of the transformation product.

This work will provide *i)* the characterization of the final products of the reactions that occur around 1200 °C for the serpentine minerals and cement-asbestos, *ii)* the characterization of possible transition phases, *iii)* the kinetic parameters at the dehydroxylation temperatures, and *iv)* the mechanism of the dehydroxylation process.

It is well known that one of the main problem in the study of massive serpentinites is the accurate identification of the different serpentine minerals, due to the close resemblance of their basic structures, invariably characterized by a 7 Å-spaced TO layers and to their similar chemical compositions. Moreover, the obtainment of accurate and precise quantitative figures of the actual chrysotile content is strongly complicated by the typical serpentinite textures, consisting of fine- to ultrafine-intergrowths of fibrous and not-fibrous serpentine minerals, often preventing their correct identification by conventional methods, such as X-ray diffraction or microanalytical approaches. This project on the HT transformation of serpentine minerals was also focused on the study of the products of thermal inhertization of cement-asbestos and on their possible recycling as secondary raw material.

Several spectroscopic techniques (such as Micro Raman, Micro FTIR, 57Fe- Mössbauer Spectroscopy and X-Ray Absorption Near Edge Structure) were used to integrate the preliminary X-ray diffraction and microscopic investigations on the secondary raw material described in Gualtieri *et al.* (2008) with a detailed study on the product of transformation at 1200 °C of friable chrysotile-asbestos and cement-asbestos. Moreover, this multi-analytical approach allowed to investigate the inner structure of fibres recrystallized after the thermal treatment.

After this characterization, the last but not the least challenge was to find suitable and attractive recycling solutions. In fact, this secondary raw material was added, in medium-high amounts (10-40 wt.%), to commercial mixtures for the production of clay bricks, rock-wool glasses for insulation as well as Ca-based frits and glass-ceramics for the production of ceramic tiles. The secondary raw material was also used for the synthesis of ceramic pigments and for the production of synthetic anorthite mixed with primary raw materials (kaolin, aluminium hydroxide) and boric acid as mineralizing agent.

MATERIALS AND METHODS

The investigated samples were: *i)* the three serpentine minerals, lizardite, antigorite and chrysotile; *ii)* a commercial cement asbestos used as outdoor roofing slate; *iii)* the product of the thermal transformation of cement asbestos at 1200 °C (Gualtieri *et al.*, 2008).

Lizardite sample is from dark-green, massive veins outcropping in the Monte Fico quarries (Eastern Elba, Italy; Mellini & Viti, 1994; Viti & Mellini, 1997). The average compositions of vein lizardite is $Mg_{2.79}Fe^{2+}_{0.09}Fe^{3+}_{0.07}Al_{0.07}Si_{1.91}Al_{0.09}(OH)_4O_5$ (Viti & Mellini, 1997).

The antigorite sample is a pale-green splintery veins occurring in massive serpentinites from Elba Island (Italy; Viti & Mellini, 1996). This antigorite sample has a superperiodicity of 48.8 Å, and a chemical composition of $Mg_{2.62}Fe^{2+}_{0.16}Fe^{3+}_{0.03}Al_{0.01}Si_2(OH)_4O_5$; loss of ignition (LOI) varied from 11.9 to 12.2 wt.%. SEM back-scattered electron (BSE) observations on the sieved powders revealed elongated to pseudo-fibrous antigorite lamellae, with a highly heterogeneous grain size from 8 to 60 µm.

The chrysotile sample is the standard asbestos SRM1866A, from an unspecified mine in Canada, provided by the National Institute for Standards and Technologies (NIST) which contains minor impurities of magnetite (*ca.* 0.5 wt.%). The average chemical formula of this sample, calculated from the chemical composition reported in Gualtieri & Tartaglia (2000), and considering 0.5 wt.% of magnetite content is: $(Mg_{2.88}Fe^{2+}_{0.11}Fe^{3+}_{0.05})(OH)_4(Al_{0.18}Si_{1.88})O_5$.

The commercial cement-asbestos (well described in Gualtieri & Tartaglia, 2000) is a mixture of clinochrysotile (12%), calcite, and amorphous phases.

The product of the thermal transformation at 1200 °C of cement-asbestos contains Mg-Al-anhydrous silicates and its composition is similar to a natural or low temperature clinker, richer in the elements mentioned above. The mineralogical composition was obtained by the Rietveld method. Principal mineralogical phases are akermanite (46.1 wt.%), merwinite (13.7 wt.%) and larnite (11.0 wt.%), followed by ferrite (1 wt.%). The remaining 28.3% are amorphous phases. More information on the characterization of this sample can be found in Gualtieri *et al.* (2008).

Thermal analyses (TG, DTG, and DTA) were carried out by a simultaneous differential thermal analysis with a (SDTA) Q600-TA Universal instrument at the Department of Earth Science of the University of Siena. Data were collected in air with a flow rate of 20 mL/min, over a temperature range of 20-1000 °C and with a heating rate of 10 °C/min, using an alumina crucible. The instrument was equipped with a Pfeiffer Thermostar mass spectrometer, for the detection of the masses emitted during heating (emitted gas analysis, EGA). Instrumental precision was checked by repeated collections on a kaolinite reference sample (more than 15 collections), revealing good reproducibility (with an instrumental theoretical T precision of ±0.5 °C) and theoretical weight sensitivity down to 0.1 µg.

The collected infrared spectra were registered from 4000 to 600 cm^{-1} with a 2 cm^{-1} resolution, using a Bruker FTIR VERTEX 70 spectrometer sited at Centro Interdipartimentale Grandi Strumenti (CIGS, University of Modena and Reggio Emilia). Experimental setup was: aperture 8 mm, 32 scans, velocity 10 kHz, detector DTGS with a window of KBr (8000-400 cm^{-1}).

As far as the Raman study is concerned, the measurements require no specimen preparation and, when performed in conjunction with a microscope, allow the collection of a spectrum from a bundle of fibres (Rinaudo *et al.*, 2004). Samples of raw- and thermally treated-asbestos-cement, and raw- and thermally treated-chrysotile, were studied with a Jobin Yvon HR800 LabRam m-spectrometer equipped with an Olympus BX41 microscope, an HeNe 20 mW laser working at 632.8 nm and a CCD air-cooled detector. In order to balance the signal against noise, 10 cycles of 100 scans were performed. In this work, only the Raman region corresponding to 1200-150 cm^{-1} was analysed. Data were recorded at University of Piemonte Orientale.

The ^{57}Fe-Mössbauer spectra were collected at the Earth Science Department (University of Roma "La Sapienza") on raw- and thermally treated-chrysotile, raw and thermally treated cement-asbestos and anorthite at room temperature, using a conventional spectrometer system operating in constant acceleration mode with a ^{57}Co source of nominal strength of 25 mCi in rhodium matrix, and recorded with a multi-channel analyzer using 512 channels. After velocity calibration against a spectrum of high-purity α-iron foil (25 µm thick), the raw data were folded to 256 channels. To have good statistics, about 5 million counts per channel were collected. For each sample about 100 mg were available and Fe total content was between 1 and 5 wt.%, so that the absorber was within the limits for the thin absorber thickness described by Long *et al.* (1983). The velocity range -10 to 10 mm/s was investigated to detect magnetic oxide impurities, in case they were present. The spectrum was fit using the Recoil 1.04 fitting program (Lagarec & Rancourt, 1988). Data analysis involved a curve-fitting procedure made by assuming a Lorentzian peak shape, and the statistical best fit was obtained by using the reduced χ^2 method, with uncertainties estimated on the basis of the covariance matrix. The experimental errors were estimated to be about ±0.02 mm/s for center shift (δ), quadrupole splitting (ΔE_Q) and peak width at half maximum (Γ), and ±0.5 Tesla for magnetic hyperfine field (H). The doublet and sextet areas were measured with an accuracy better than ±3%.

Transmission electron microscopy (TEM) was performed with a JEOL 2010 microscope, sited at Earth Science Department of University of Siena, working at 200 kV and equipped with an Oxford ISIS energy-dispersive X-ray spectrometer (EDS).

X-ray powder diffraction patterns were collected using a Panalytical X'Pert Pro, available at CIGS (University of Modena and Reggio Emilia). This instrument, with θ/θ geometry, CuKα radiation, and an RTMS (Real Time Multiple Strip) detector, allowed to acquire *in situ* and *ex situ* data.

The Rietveld analysis of *ex situ* powder data was conducted to determine the phase association and the amount (wt.%) of both the crystalline and amorphous phase content at various temperatures.

Finally, part of the doctoral work was focused on the use of non conventional techniques. Data for X-Ray Absorption Spectroscopy (XAS) and X Ray Powder Diffraction were collected at the European Synchrotron Radiation Facilities (ESRF). Absorption data were acquired in May 2009 during a shift at BM08 GILDA beamline; diffraction patterns were respectively collected in May 2011 at BM08, and in October 2011 at BM01, the Swiss Norwegian Beamline.

RESULTS

Quantitative determination of chrysotile in massive serpentinites using DTA

Thermal analysis was confirmed to be a valid method for the qualitative discrimination of serpentine minerals, due to the occurrence of systematic differences in dehydroxylation mechanisms and temperatures of chrysotile (Ctl), antigorite (Atg) and lizardite (Lz) (Viti, 2010). Overall results point to a good linear correlation between peak area ratios (of both Lz/Ctl and Atg/Ctl) and chrysotile content (wt.%); the corresponding calibration curves are shown in Fig. 1a and Fig. 1b (for lizardite and antigorite, respectively). The linear

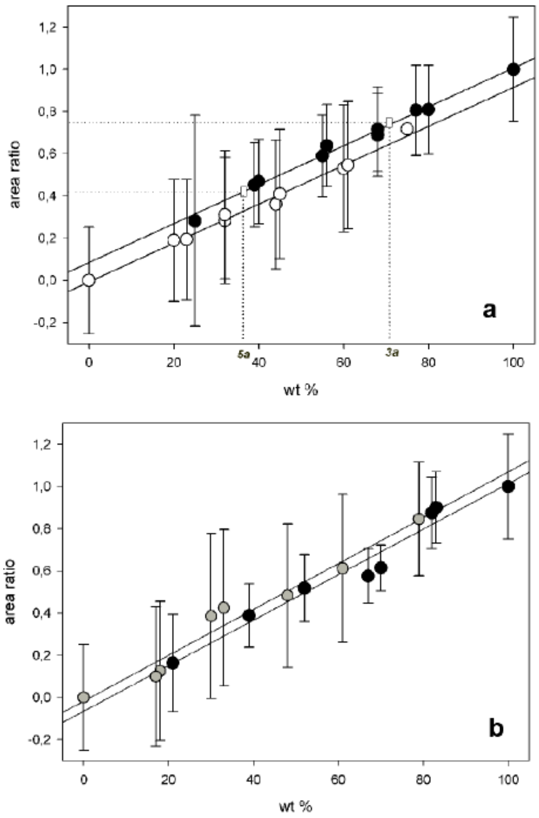

Fig. 1 - Correlation curves between total area ratio and chrysotile amount (wt.%) for Lz + Ctl (a) and Atg + Ctl (b) samples; standard error associated with each measure is represented by error bars. Legend: black dots = Lz; gray dots = Atg; white dots = Ctl; white squares = the two investigated unknown samples 3a and 5a.

regression for lizardite data was fairly good ($R^2 = 0.9903$) and the calculated equation was $y = 0.0922x - 0.0704$; for antigorite, was $R^2 = 0.9609$ with the following calculated equation: $y = 0.0108x - 0.016$.

The applicability of the above DTA calibration curves has been tested on two representative massive serpentinites from Elba Island (samples 3a and 5a in Viti & Mellini, 1997). Quantitative DTA peak analysis revealed that sample 3a is definitely richer in chrysotile than sample 5a (~ 70 and 35 wt.%, respectively, on the basis of our calibration curve for Lz + Ctl samples) (Fig. 1b). These results are in good agreement with the previous results obtained by the Rietveld method, confirming the suitability of the method.

The dehydroxylation of serpentine group minerals

The aim of this part of the thesis was the study of the high temperature reaction of the serpentine minerals, their stability fields, and their reaction kinetics to draw a comprehensive model of their dehydroxylation and recrystallization reactions. Below are described some of the most relevant results.

In all the three serpentines the first reaction is the decomposition of the starting phase followed by the formation of forsterite, above 650 °C, and enstatite, above 825 °C (see Fig. 2).

Talc was not observed, probably because of the low number of counts during data collection. Rietveld refinements on *ex situ* data were collected on thermally treated chrisotile, lizardite and antigorite (heated at 750-775-800, 1000 and 1200 °C, respectively). Rietveld refinements confirmed the presence of talc as metastable phases in antigorite (Fig. 3) and less obviously in lizardite. Chrysotile is stable up to 750 °C, lizardite up to 775 °C and antigorite decomposes at 800 °C.

Talc was observed as metastable phase in antigorite and, to a minor extend, in lizardite. When the heating rate was fast (that is > 30 °C/min), the talc-like phase was not observed. When the heating rate was slower (< 30 °C/min), the talc-like phase was observed. Regardless the rate of heating, talc was never observed in chrysotile indicating both a crystal chemical (thermodynamic) and kinetic control of the reaction. Kinetic analysis allowed us to demonstrate that the rate-limiting step of chrysotile dehydroxylation is the one-dimensional diffusion in the interlayer region along the fibre axis with an instantaneous or decelerator nucleation rate. The rate-limiting step of dehydroxylation of lizardite was the deceleratory nucleation and the two-dimensional diffusion, whereas that of antigorite suggested a mechanism with a deceleratory nucleation rate and one-dimensional diffusion. For lizardite, the Avrami coefficient was compatible with three possible reactions steps or with a combination of them, as proposed in Gualtieri *et al.* (2012).

The three serpentine polymorphs exhibited different dehydroxylation apparent activation energies (E_a): $E_a = 184$ kJmol^{-1} for chrysotile; $E_a = 221$ kJmol^{-1} for lizardite; $E_a = 255$ kJmol^{-1} for antigorite. These values are comparable to the E_a calculated for the dehydroxylation of brucite (*i.e.*, 210-238 kJmol^{-1}) although a totally different mechanism (phase boundary controlled reaction) was postulated.

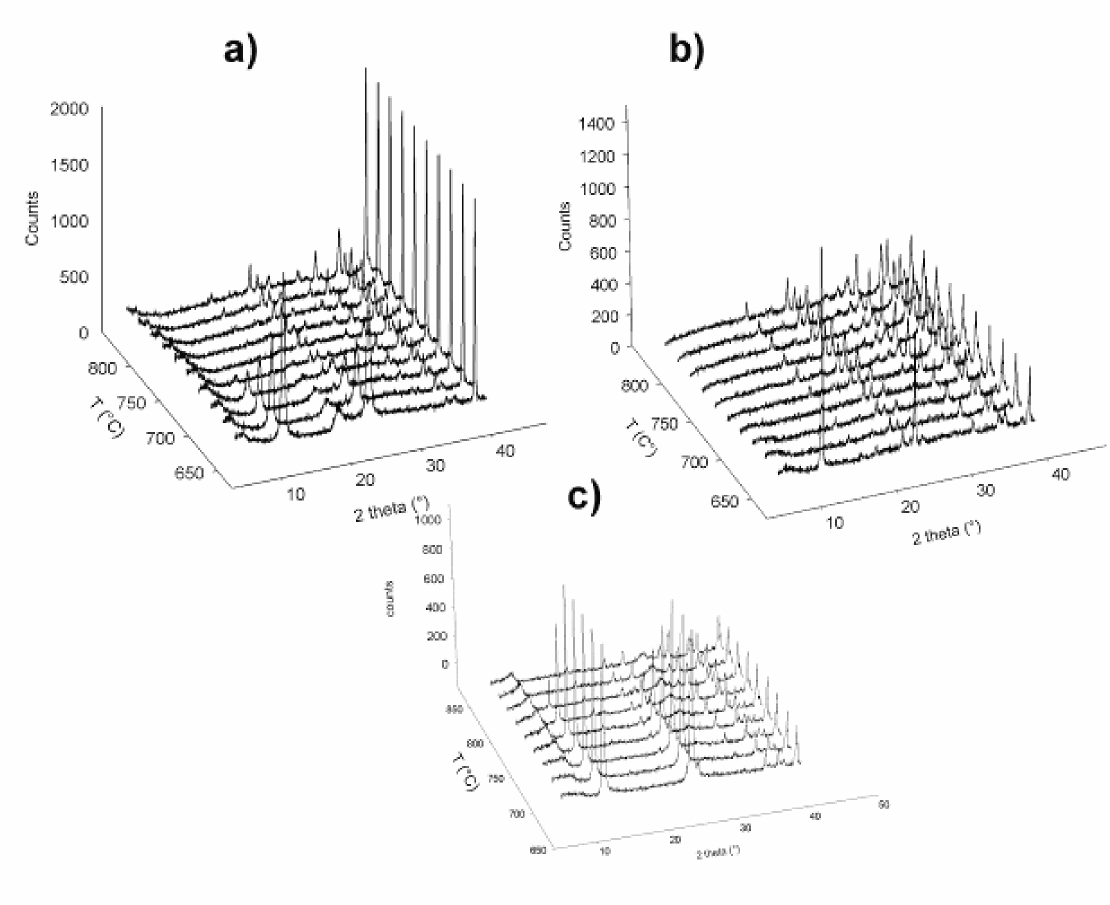

Fig. 2 - Dynamic XRPD experiments on antigorite (a), lizardite (b) and chrysotile (c).

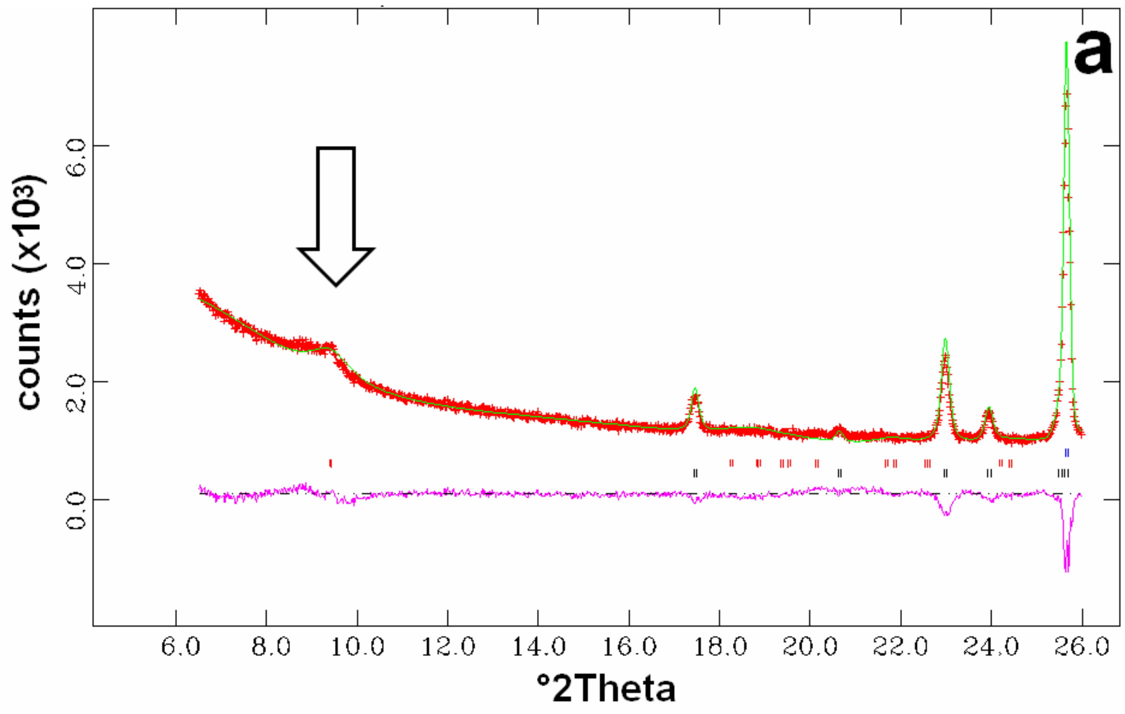

Fig. 3 - Graphical output (observed, calculated and curve of the differences) of the Rietveld refinement for the quantitative phase analysis of antigorite heated at 800 °C.

Spectroscopic study of the product of thermal transformation of chrysotile-asbestos containing materials (ACM)

On the basis of the micro-Raman and FT-IR spectra it was possible to rule out the presence of untransformed core within asbestos fibres either in the high temperature products of transformation of friable asbestos and cement-asbestos. Hence, it was possible to claim that a complete solid state transformation has regarded all the asbestos fibres in the original material.

Opposite to the statistical result obtained by the X-ray quantitative phase analysis, which evidenced the presence of clinker related newly-formed phases (akermanite, merwinite, ferrite, and others), in the overall transformation product of cement-asbestos, micro-Raman, with its local nature, showed that the main transformation product of the core of the fibres was forsterite. The study with Mossbauer spectroscopy showed that chrysotile contains both Fe^{2+} and Fe^{3+} in octahedral coordination. The 1200 °C product of standard chrysotile revealed the presence of magnetite/maghemite and hematite. Raw cement-asbestos contains both Fe^{2+} and Fe^{3+} in octahedral coordination, whereas thermally treated asbestos cement contains Fe^{3+} in a tetrahedral coordination.

XANES spectra showed that in all samples the dominant iron oxidation state is 3+. XANES data on standard chrysotile are compatible with the presence of magnetite. In the secondary raw material, the high intensity of the pre-edge peak is comparable with that of the reference compound Fe-silicalite, with ferric iron hosted in the tetrahedral framework. This result indicates that ferric iron is likely inside a crystalline phase in four-fold coordination, in agreement with Mössbauer spectroscopy results. Such crystalline phase could be Fe-bearing akermanite-gehlenite (melilite).

Recycling of the product of thermal inertization of cement-asbestos for various industrial applications

After the characterization of the thermally treated cement asbestos and the reassurance of its non-hazardous nature by means of spectroscopic methods, in this part of the PhD work the recycling solutions for the secondary raw material were evaluated. Recycling of thermally treated asbestos-containing material in traditional ceramics has already been successfully studied. Previous work by Gualtieri *et al.* (2008) showed that this secondary raw material can be successfully recycled in the production of stoneware tiles or for the production of the concrete (Gualtieri & Boccaletti, 2011). The products were fully characterized with physical, rheological, mechanical, and thermal tests as fully described in Gualtieri *et al.* (2011a). The characterization followed the common practice for quality control, and was executed according to the existing tests for the characterization of polymers by the ASTM International. The results of the addition of thermally treated cement-asbestos, in place of calcite, gave very promising results. In fact, the rheological, mechanical, thermal, and technological properties were very similar to those of the standard.

The final colour of the product is brown due to the relatively high iron content in our secondary raw material. Hence, the use of thermally treated cement-asbestos as filler is limited to materials which are destined to have a dark colour. Thermally treated cement asbestos was also used for the production of synthetic anorthite (Gualtieri *et al*., 2011b).

CONCLUSIONS

The purpose of this thesis was the study of the high temperature reactions of the serpentine group minerals and the characterization of the product of the thermal treatment of asbestos-cement in a view of a possible recycling of the transformation product. The characterization of the metastable and final phases occurring in serpentine minerals at the dehydroxylation temperature and at 1200 °C was possible using a combined analytical approach by means of HRTEM observation and *in situ* and *ex situ* XRPD; this approach permitted: *i)* to understand the nature and stability field of metastable phases, *ii)* to characterize the final product of the high temperature reaction, *iii)* to find the kinetic parameters, and *iv)* to describe the mechanism of the dehydroxylation process. As far as the *ex situ* experiments were concerned, antigorite, heated at 800 °C, and lizardite heated at 775 °C, clearly showed the presence of a metastable talc-like phase, together with forsterite and an amorphous phase. Moreover, it was possible to claim that slower rates of dehydroxylation favour the conservation of residual hydroxyls within the layers prompting the nucleation of the talc-like phase in antigorite, and, less, in lizardite; in particular when the heating rate is fast (*i.e.*, > 30 °C/min), the talc-like phase was not observed, whereas, when the heating rate is slower (*i.e.*, < 30 °C/min), the talc-like phase was observed. Dehydroxylation reaction kinetics were also studied on the three samples. The application of "Avrami method" allowed to determine the serpentine dehydroxylation process. With an Avrami coefficient of $n = 0.61$, it was postulated that the rate limiting step of chrysotile dehydroxylation is one-dimensional diffusion with an instantaneous or decelerator nucleation rate (Cattaneo *et al.*, 2003). The average Avrami coefficient ($n = 1.6$) obtained in this work for the dehydroxylation of lizardite indicates that the rate-limiting step of the reaction is deceleratory nucleation rate and two-dimensional diffusion (Hulbert contribution in Bamford & Tipper 1980); the average Avrami coefficient ($n = 0.8$) obtained in this work for the dehydroxylation of antigorite points to mechanism with a deceleratory nucleation rate and one-dimensional diffusion. The three serpentine polymorphs exhibited also different dehydroxylation apparent activation energies. This has important implications for the understanding of the subduction zone water cycle with special attention to the dehydration induced by the subduction of the oceanic lithosphere.

The applicability of thermal analysis for quantitative determination of serpentine minerals was confirmed. In fact, DTA analysis resulted a suitable method for the qualitative and quantitative discrimination of serpentine minerals, due to the occurrence of systematic differences in dehydroxylation mechanisms and temperatures of chrysotile, antigorite, and lizardite. The work conducted on this topic demonstrated that thermal analysis is a very promising method for the quantitative determination of the chrysotile content within complex samples such as massive serpentinites, with obvious implications in asbestos-related issues. The method here proposed has several advantages with respect to currently-employed methods for quantitative asbestos determinations (*e.g.*, fibre counting on known aliquots through microscopic approaches), in terms of accuracy, precision, inter-laboratory transferability and time/cost benefit. Together with the relatively good accuracy/precision in both qualitative and quantitative determinations, the present method provides other significant advantages, such as *a)* the high sensibility (detection of very low amount of chrysotile), *b)* the limited instrumental and experimental costs, *c)* the relatively short time required for quantitative determinations (especially if compared with fibre counting methods by phase-contrast optical microscopy, SEM or TEM), and *d)* the straightforward inter-laboratory transferability. Even if further calibrations, tests and experimental improvements should be required for a better definition of the method and of possible drawbacks, we can conclude that thermal analysis appears to be one of the most promising tools for chrysotile quantitative determinations, providing relatively fast, poorly expensive and accurate responses to recent asbestos-related law requirements.

The results obtained with spectroscopic techniques ruled out the presence of untransformed core within asbestos fibres in both the high temperature products of transformation of friable asbestos and cement-asbestos and permitted to claim that a complete solid state transformation has regarded all the asbestos fibres of the original material. In fact, the collected Micro-Raman and micro-FTIR spectra showed that the core of thermally treated fibres is fully transformed. As a matter of fact, the absorption bands generated by the asbestos minerals are no longer present. Olivine and enstatite are the newly-formed phases in the core of the relics of friable asbestos, whereas olivine is accompanied by other phases in the product of transformation of cement-asbestos, such as hematite and (Ca, Mg, Al)-silicates

The study with Mössbauer spectroscopy showed that raw cement-asbestos contains both Fe^{2+} and Fe^{3+} in octahedral coordination, whereas the thermally treated cement asbestos contains Fe^{3+} in a tetrahedral coordination. In this sample, the high intensity of the pre-edge peak is comparable with that of the reference compound Fe-silicalite, with ferric iron hosted in the tetrahedral framework. This result indicates that ferric iron is likely inside a crystalline phase in 4-fold coordination, and that this crystalline phase could be Fe-bearing akermanite.

The last challenge was to find the potential applications of thermally treated cement asbestos as secondary raw material. This product could be recycled in traditional ceramic, for the production of clay bricks, rock-wool glasses for insulation, as well as for the synthesis of anorthite. Positive results have been obtained regarding the manufacture process of clay bricks using thermally treated cement asbestos as secondary raw material. By the addition of this material to the standard clay, good values of linear firing shrinkage and modulus of rupture were obtained. Moreover, two pigments were synthesized and characterized, and one of them is especially interesting for the ceramic industry due to its thermal stability (up to 1300 °C). Our secondary raw material was also successfully used as filler in plastics, without altering the properties of the final product compared to standard fillers and for the production of synthetic anorthite. The colour of this anorthite is fairly white due to the absence of iron oxides, and this suggests its possible utilization as white pigment for traditional ceramics.

In conclusion, asbestos was a natural source that turned into a problem; now it is possible to turn back the problem into a source. It is important to highlight that this project is fully in line with the European Directives for Environment protection and:

1) it offers a conclusive solution to the asbestos-problem;

2) landfills for disposal of asbestos containing wastes would be no longer needed because the product of transformation of asbestos containing wastes can be recycled as a safe secondary raw material;

3) the secondary raw material can be used in place of natural raw materials (such as calcium carbonate) thus reducing the exploitation of natural resources and their environmental impact;

4) the product of transformation of asbestos containing wastes, and especially the cement-asbestos, is a potentially important CO_2-free source of calcium (and silica) for various products such as cements and ceramic pigments. The use of this secondary raw material as Ca source instead of $CaCO_3$ (normally used) eliminates the energy-consuming decarbonation step and also reduces the CO_2 emission.

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