



Influence of trace elements on the textural properties of synthetic chrysotile: Complementary insights from macroscopic and nanoscopic measurements



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ABSTRACT

The present study shows that the presence of Li, Sb, As and B as trace elements significantly influences textural properties such as particle size distribution, morphology and specific surface area of chrysotile synthesized under hydrothermal conditions ($P = 8.2$ MPa, $T = 300$ °C and high-alkaline pH (13.5)). Conversely, traces of Cs did not have any textural effect under these conditions. Furthermore, chrysotile nanotubes size and morphology depend strongly on the element considered. Indeed, large chrysotile with cylinder in cylinder morphology (outer diameter up to 50 nm) precipitated in the presence of Li, Sb and As. This implies lower specific surface area (124 – 160 m² g⁻¹) compared to undoped chrysotile (184 m² g⁻¹ with about 14 nm in width). The presence of boron favors the precipitation of thin fibrous nanotubes similar to undoped chrysotile in width, but significantly longer, with tubes length that can reach three microns in length. In this case, the specific surface area increase slightly from 184 to 196 m² g⁻¹. The solid–liquid partition coefficient for each investigated trace element was determined using Langmuir equation. This well-tubular geo-material can be used as a model to better understand the effects of trace elements on the precipitation of minerals that are relevant in Earth systems (e.g., serpentinization processes) and societal applications (e.g., asbestos toxicity and CO₂ sequestration).

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1. Introduction

The formation and textural properties of serpentines (i.e., chrysotile, lizardite and antigorite) have already been investigated in the past. However, various questions still remain unanswered, especially concerning their crystallization in natural and experimental systems and the textural effects of foreign ions during their formation was hardly investigated. Chrysotile is made of a succession of concentric or spiral layers with a fivefold symmetry [1–3] forming a nanometric tubular structure with several polymorphs [4–7]. Beyond a critical size (width >100 nm) chrysotile becomes unstable and polygonal serpentine is observed [8,9]. The complexity of chrysotile fibrils structure and morphology makes careful experimental work and nanoscale investigation absolutely essential. Serpentine has been experimentally synthesized for decades [10,11]. Authors were especially interested in the kinetics and

stability domains of serpentine polymorphs (lizardite, chrysotile and antigorite) [12,13]. Recently, new experimental protocols have been developed for synthesizing pure homogeneous chrysotile [13–15] and it has become possible to properly investigate the effects of physico-chemical parameters on various properties (texture, thermal stability, kinetics) of chrysotile. These effects are of prime importance since the textural properties (size, morphology, specific surface area) largely influence the reactivity of chrysotile [14,15]. Optimal synthesis protocols have been set up to study health hazards of asbestos mineral [15,16]. Chrysotile synthesis is favored for a high pH (>13) and temperatures between 300 and 400 °C [17,18]. The longest chrysotile nanotubes are formed around 400 °C after 168 h of reaction [17] and the highest chrysotile crystallinity is obtained at pH > 13 in NaOH medium which promotes the incorporation of –OH [18] or using mineralizing agents [19]. Results indicated that synthetic chrysotiles rarely exceed 30 micrometers in length [20] whereas natural chrysotile fibers showed lengths ranging from few nanometers to several centimeters [4,21]. The influence of Mg-substitution has also been investigated to characterize the role of major (Fe) and minor (Ni, Ti,

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Co) elements on the thermal and textural properties of synthetic chrysotile (size and morphology) and on the kinetics of chrysotile formation [16,22].

Both cationic substitution and the presence of impurities have direct implications on atomic bonds and affect the unit-cell geometric parameters of crystals. Consequently, previous studies have indicated that chrysotile nucleation and growth is strongly affected by the presence of major or minor elements (e.g., Fe, Ni, Co) in solution [23–26]. This induces the precipitation of chrysotile particles with complex cylinder in cylinder [27,28], cone-in-cone [25] and/or spiral morphology [29]. Chrysotile synthesized in the presence of Fe-doped solution has a lower thermal stability [22] and faster formation kinetics [30]. Nanotube cores have diameters of about 5–8 nm [31] and a previous study indicated that this particular geometry could favor the sequestration of trace elements such as Li in the hollow center of the nanotubes [32]. Serpentine is an important carrier of fluid mobile elements (e.g., Li, B, Sb, As, Cs, Sr, Pb) in natural settings [33,34]. Thus, understanding the sequestration of these trace-elements during serpentine formation is necessary and can be achieved by experimentation. In the same way, it is important to clearly identify the influence of single- and multi-element systems on the macroscopic and nanoscopic properties of chrysotile. For that purpose, an experimental investigation is crucial to quantify single trace element partitioning during chrysotile precipitation and evaluate the resulting influence of each element on the chrysotile textural properties at all scales.

We based our approach on a published protocol for undoped synthesis ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) [35]. Trace-element-doped chrysotiles were then synthesized by alternatively adding Li, As, B, Sb or Cs at different concentrations. We estimate that the chemical compositions of the synthetic solids are in equilibrium with the solution after 30 h of reaction. Our goal is twofold. We first determine the effects of the above-mentioned trace elements on the textural properties of chrysotile and then provide new data on the partitioning of trace elements between fluid and solid during chrysotile formation. Geochemical measurements on bulk solid product were carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Chrysotile products were characterized from macroscopic to nanoscopic scale by performing N_2 adsorption isotherms measurements, ThermoGravimetric Analyses (TGA/SDTA), Field Emission Gun Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM).

2. Methods

2.1. Chrysotile synthesis

Syntheses of chrysotile doped with a single trace element were performed using 1.302 g of commercial silica gel (H_2SiO_3 provided by ROTH) and 5.082 g of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ provided by ROTH) used without any treatment and mixed in 250 ml of 1 M NaOH solution doped with one single trace element at various concentrations placed in a *Parr copper alloy* reactor (autoclave with internal volume of 0.5 L). The trace element concentrations experienced were 5, 20, 50, 100, 200 $\mu\text{g g}^{-1}$ for Li, Sb, Cs, B and As elements, and 500 and 1000 $\mu\text{g g}^{-1}$ in addition for As. This aqueous reactive system was immediately stirred using constant mechanical agitation (300 rpm) during the reaction. The aqueous system was then heated at 300 °C for 30 h using a heating jacket adapted to the reactor, following preliminary experiments on chrysotile syntheses.

At the end of each experiment, the autoclave was removed from the heating system and immersed in cold water. After water cooling down to 30 °C (about 15 min) the autoclave was disassembled, and the solid product was carefully recovered and separated by

centrifugation (20 min at 11,500 rpm), decanting the supernatant solutions. The solid product was washed two times by re-dispersion/centrifugation processes in order to remove soluble compounds (e.g., NaCl and Na_2CO_3) co-formed during synthesis and adsorbed trace elements. Finally, the solid product was dried 90 °C for 48 h and preserved in dry environment for further characterizations (TGA, N_2 adsorption isotherms, FESEM and TEM).

2.2. Analytical procedure

2.2.1. N_2 sorption isotherms

N_2 sorption isotherms were performed for several runs using a Micrometrics ASAP 2010 system. The specific surface area for 100 mg of powdered samples was estimated from the Brunauer–Emmet–Teller (BET) equation in the $0.05 \leq P/P_0 \leq 0.35$ interval of relative pressure and using 16.2 \AA^2 for cross-sectional area of molecular N_2 . Additionally, the Barrett, Joyner, and Halenda (BJH) method [36] taking into account the capillary condensation using the Kelvin equation was used for the determination of the pore size distribution.

2.2.2. FESEM and TEM observations

Micro-imaging was carried out on a Zeiss Ultra 55 Field Emission Gun Scanning Electron Microscopy (FESEM) in order to evaluate the serpentine grain size and morphology. The spatial resolution is approximately 1 nm at 15 kV. Solid samples were dispersed by ultrasonic treatment in absolute ethanol for at least 5 min in order to disaggregate the particles. One or two drops of solution were placed on an aluminum support and coated with a thin film of platinum for SEM observation. Additionally, our samples were scattered for short times in ethanol in order to split the aggregates without any additional treatment. An ethanol drop of the chrysotile suspension was deposited on a holey carbon foil placed on conventional copper micro-grids for further observations with JEOL 2100F Transmission Electron Microscope (TEM) operating at 200 kV, equipped with a field emission gun and a high-resolution pole piece achieving a point-to-point resolution of 1.8 Å. Chemical mapping was achieved by combining the scanning module of the microscope (STEM) to the EDS detector. To try and resolve trace elements, acquisitions were conducted for more than two hours. None of the investigated trace elements were detected by EDS in serpentine, but we were able to resolve the occurrence of oxide precipitation containing high amounts of these elements.

2.2.3. Thermogravimetric analyses (TGA)

TGA for experimental solid products was performed with a TGA/SDTA 851^e Mettler Toledo instrument under the following conditions: sample mass of about 10 mg, platinum crucible of 150 μl with a pinhole, heating rate of 10 °C min^{-1} , and inert N_2 atmosphere of 50 ml min^{-1} . Sample mass loss and associated thermal effects were obtained by TGA/DTGA in a temperature range of 30–1200 °C with an accuracy of about ± 0.25 °C.

The melting points of three compounds (indium, aluminum and copper) obtained from the DTGA signals were used for sample temperature calibration. Calcium oxalate was used for mass sample calibration. Weighting accuracy is 0.1 μg , which correspond to 0.01% for a 10 mg sample.

2.2.4. Trace element concentrations measurements

Li concentrations were determined at the Laboratoire d'Hydrologie et de Géochimie de Strasbourg (LHyGeS) by ICP-MS using a Thermo Finnigan X series II. Sb, As and Cs were determined by ICP-MS using an Agilent 7500ce at ISTERre laboratory (Grenoble, France). For Li, about 150 mg of sample was crushed in an agate ring mill before acid digestion by HF and HNO_3 . The complete analytical procedure is described in [37]. The same procedure, using

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