Sequestration of trace elements during nucleation and growth of serpentine minerals under hydrothermal conditions

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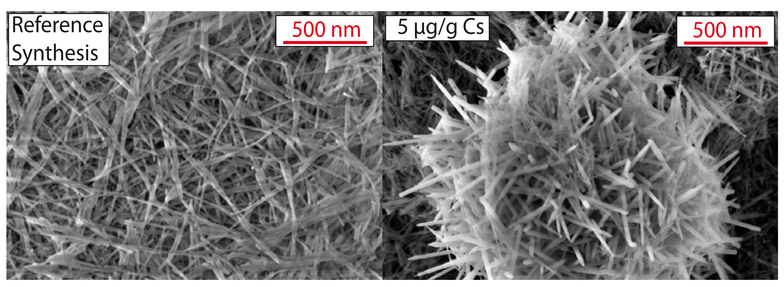
Introduction

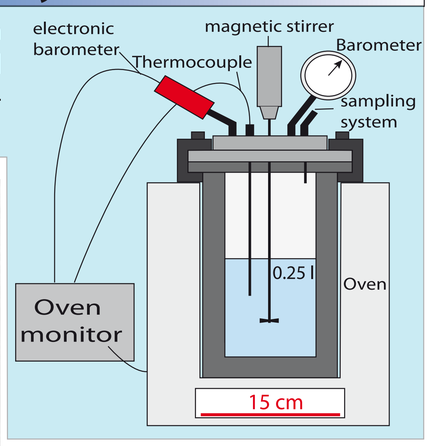
Serpentinization occurs in ocean mantle due to interaction between olivine and fluids. Serpentine resulting from this reaction generaly contains high concentration of fluid-mobile-elements (FME) relative to primitive mantle. Those elements (As, B, Cs, Li, Sb) represent excellent marker of mass transfert in complex geodynamics systems.

In this study we developed two methods involving different mechanisms of nucleation and growth for serpentine. We measured reaction advancement and influence of FME with several analytical methods (TGA, FTIR, FESEM, XRD) and propose a kinetic model describing reaction advancement.

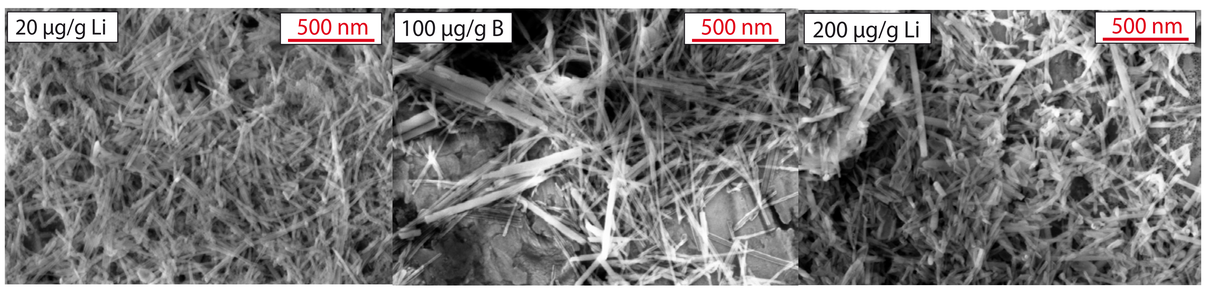
Chrysotile synthesis «silica-gel system»

Serpentine nanofibers of chrysotile were nucleated-grown from H_3SiO_2-$MgCl_2$-NaOH hydrothermal system, referred as «silica-gel system» (300°C, Mg/Si=1.5, 76bar and pH>13) in autoclave. Morphology of synthesis products was characterized using FESEM.

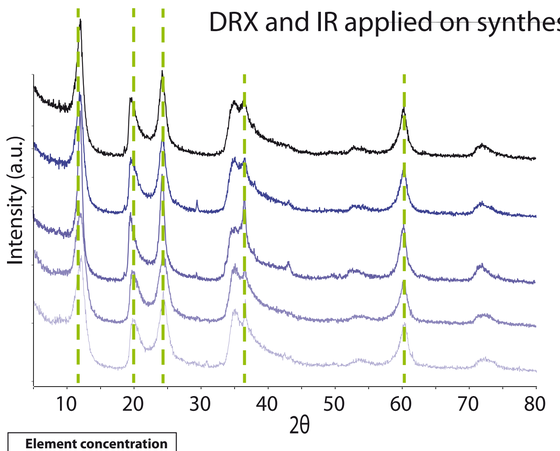


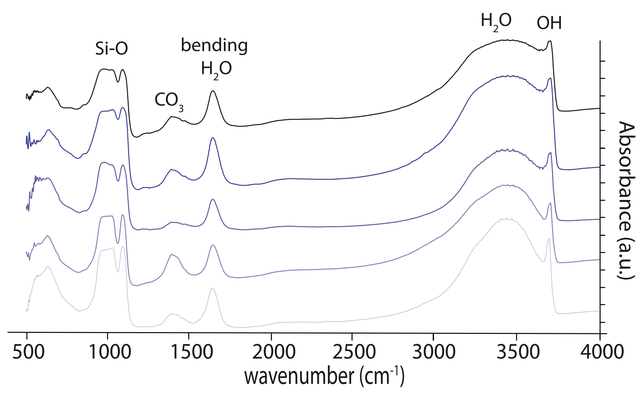


These conditions allow the formation of single serpentine with no brucite or talc. Influence of trace elements on structure and morphologies was controlled for solution doped in one single trace (B, Li, Cs, Sb or As) at concentrations of 5, 20, 50, 100 and 200 µg/g .



DRX and IR applied on synthesis products dopped in trace elements **(Li exemple)**.



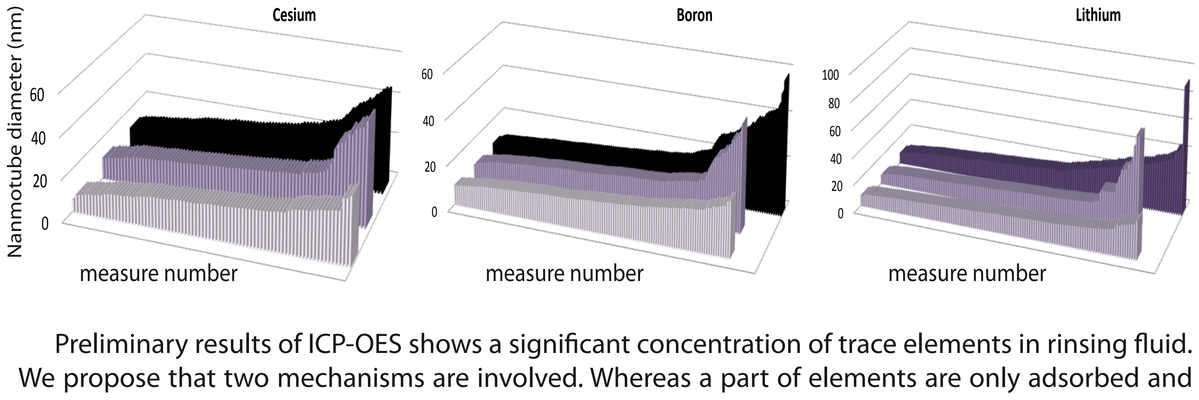


Element concentration in starting fluid
- 200 µg/g
- 100 µg/g
- 50 µg/g
- 20 µg/g
- 5 µg/g

FTIR and XRD analyses reveal no physical properties change.

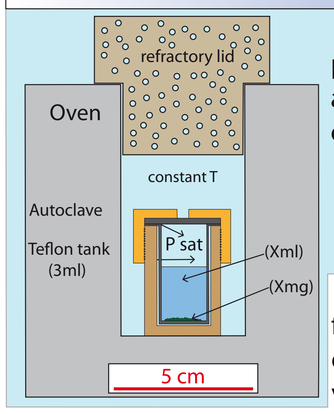
Morphology and size of serpentine nanotubes seem to be influenced by trace elements incorporation. Image processing reveals one unique family of chrysotile nanotubes with average diameter of 16±3 nm and 430±30 nm in length for fluid concentration lower than 20µg/g.

Larger cylinder in cylinder particules are observed in highly doped synthesis.



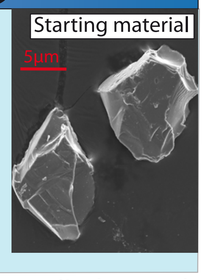
Preliminary results of ICP-OES shows a significant concentration of trace elements in rinsing fluid. We propose that two mechanisms are involved. Whereas a part of elements are only adsorbed and easily remobilised, the other part seems incorporated into structure. This will be confirmed by XAS measurements.

Alteration «Olivine system»

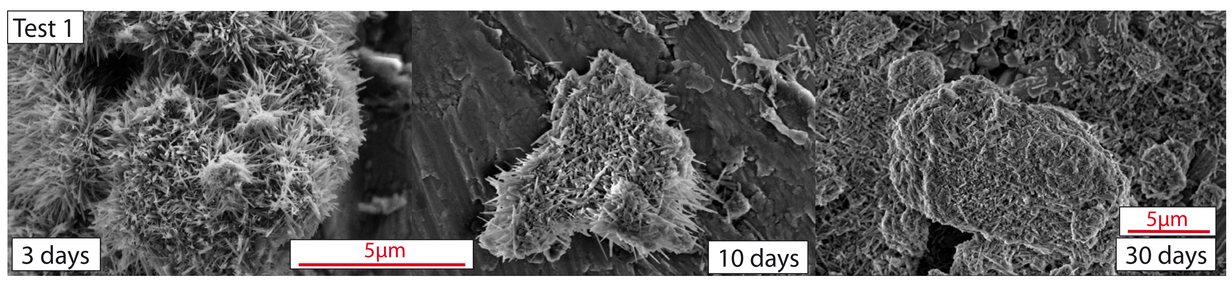


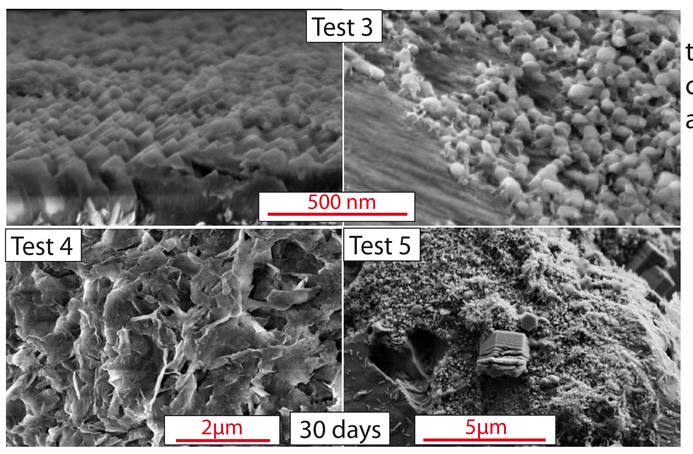
Small static-batch reactors were used to simulate serpentinization hydrothermal conditions. Olivine (San Carlos) alteration was investigated at different physicochemical conditions.

# test	pH solution	Temperature °C	time	f/s weight ratio
1	13,5	200	3h to 60 days	15
2	13,5	200	30 days	5
3	5,8	200	30 days	15
4	0,7	200	30-60 days	15
5	13,5	150	30-60 days	15

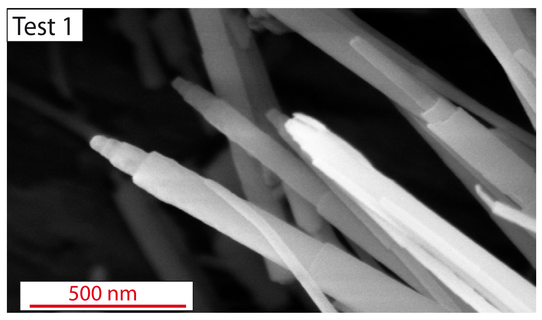


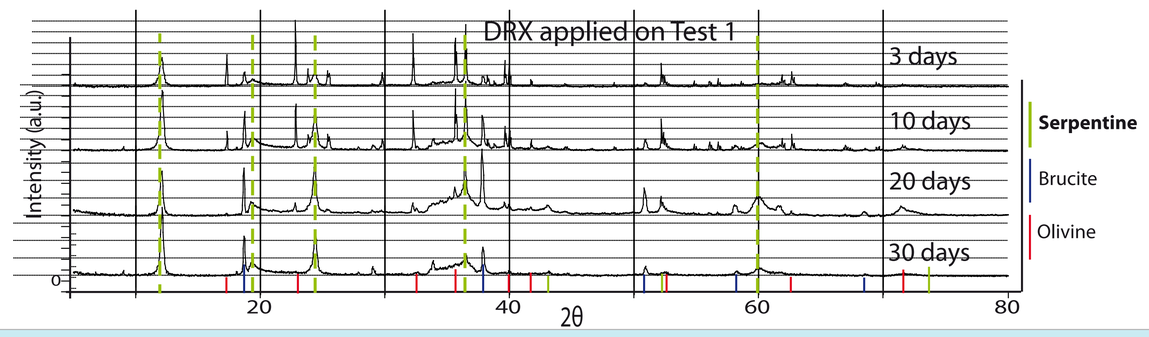
Three nanocrystal morphologies (conical, cylinder in cylinder and fibrous) of chrysotile and associated brucite nanoparticles were clearly observed at high pH (>13). Conversely, slight alteration of olivine was observed at low pH (<2) or at low temperature (150°C) with the same parameters.





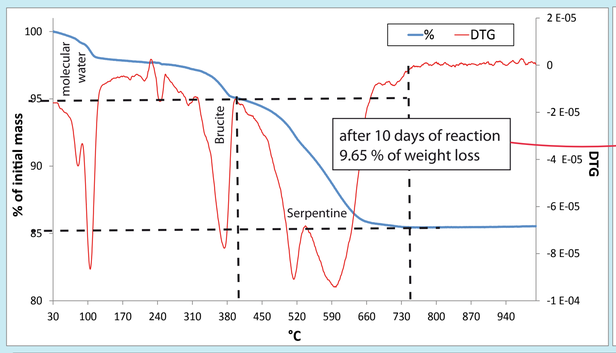
Alteration features were observed for neutral conditions where serpentinisation process is the slowest. Nucleation of serpentine at olivine surface is well identifiable.

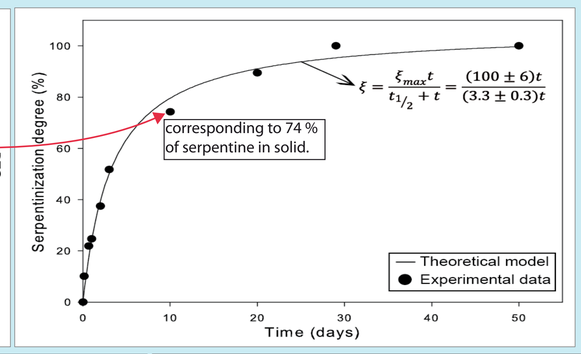




Kinetic model

The serpentinization kinetics is estimated for alcaline system by TGA and DTG following:
$2Mg_3Si2O_5(OH)_4 = 3Mg_2SiO_4 + \mathbf{4H_2O} + SiO_2$ XRD after TGA has revealed enstatite and forsterite composition.





Serpentinisation begins fast due to prompt dissolution of olivine and rate decreases after 5 days (60% serp) following kinetic pseudo-second-order model. Ratio between OH band and SiO band is systematically estimated. There is a linear relationship between this ratio and the serpentinization. This enables to estimate the kinetic rates from the FTIR spectra.

Conclusions and Perspectives

An innovative and simple synthesis protocole has been developed. It allows the formation of pure serpentine without secondary phases and additive use. By this approach, we are able to determine trace elements influence on nucleation and growth of serpentine.

Preliminary results by FESEM reveal that the presence of trace elements has significant effect on chrysotile nanofibres morphology and size grown from «silica-gel system». We observed a transition from an unique fiber morphology to complex morphologies like in «olivine system», and an increase of particle size.

Olivine alteration was investigated for differentc onditions of pH, T, durations and fluid/solid mass ratio. At basic conditions, olivine alteration in chrysotile and brucite has the fastest kinetic . Serpentinization kinetic was determined from TG. We also established a calibration curve between the OH/SiO bands in FTIR and the degree of serpentinization.

Further experiments and trace element analyses in the solid will allow us to best understand sequestration of trace element depending of the serpentinisation conditions and measure the incorporation

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