

Serpentine dehydroxylation: a multi-analytical approach using TGA, XRD and Vibrational Spectroscopy

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Serpentinites and serpentine-bearing rocks are ubiquitous on Earth and contain an extended set of economically important elements which make them of interest for the mining industry. Notwithstanding, serpentinites play a crucial role in the recycling of lithospheric plates as their stored water which is lost during subduction acts as a trigger for active magmatism along convergent plate boundaries such as along the American Cordillera. The transformation behaviour of their main constituents is thus a beneficial field in Earth Sciences since long. However, most studies focus on high temperature-high pressure studies of a complex paragenesis, i.e. rocks, although a fundamental understanding of the mineral breakdown reactions has long been lacking or is still a matter of debate.

Serpentinites are predominantly made of serpentine minerals, i.e. lizardite, chrysotile and antigorite, a group with a common stoichiometry of $Mg_3Si_2O_5(OH)_4$, but differing crystal structure. The latter property makes them to a material of choice when interested in a study focussing on structure-dependent phase transformation reactions. In general, serpentine minerals are trioctahedral 1:1 phyllosilicates with a hexagonal arrangement of SiO_4 tetrahedra forming the T-sheet which is linked by sharing their apical oxygens with octahedrally coordinated magnesium within the brucite-like O-sheet. Looking at the crystallographic *b* direction there is a mismatch between both sheets which can be alleviated by a series of chemical and crystallographic modifications, which give rise to the serpentine polymorphs (Wicks and O'Hanley 1988). Lizardite is a flat lying modification showing a crystal structure similar to that of kaolinite whereas chrysotile forms nano-fibres with enrolled TO layers and a variable inner and outer diameter. The dehydroxylation temperature in nanotube-like chrysotile is radius dependent and will be higher in the innermost layers compared to the less curved outer parts of the chrysotile fibres.

The phase transformation reaction of two of these serpentine minerals, i.e. lizardite and chrysotile, were studied in detail by an extended set of analytical techniques and with a focus on the dehydroxylation kinetics. The sample material was characterised with respect to chemistry, crystallography, thermoanalytical behaviour and particle size by means of electron microscopy, electron microprobe, X-ray powder diffraction, FTIR and Raman spectroscopy, thermogravimetry and partly by BET analysis prior to phase transformation experiments (Trittschack 2013).

In advance, two detailed micro-FTIR and micro-Raman studies focussing on the high-temperature breakdown reaction of lizardite and chrysotile, respectively, were done on the sample material in order to build up a solid base for the kinetic interpretation. Results coming from in situ high-temperature X-ray powder diffraction and thermogravimetry supplement the interpretations of vibrational spectroscopy and vice versa. Both minerals were examined between room temperature and around 850°C under non-isothermal conditions by means of FTIR and Raman spectroscopy as well as thermogravimetry. X-ray studies were performed under isothermal conditions only.

Lizardite and chrysotile alike are characterised by a breakdown reaction with an almost X-ray amorphous, but still OH containing talc-like intermediate phase as recognizable from Raman spectra. The quantitative amount and the temperature range of its presence are dependent on crystallographic properties, but heating conditions also. Chrysotile dehydroxylation is characterised by a much broader temperature range in comparison to lizardite which can be interpreted as a result of the radial structure. Dealing with reaction kinetics in Geosciences is not new, but the majority of articles dealing with kinetics on phase transformations and published after 2000 are still using old fashioned model fitting approaches which are going back to the 1960s and 1970s. Thus, isoconversional methods have found a few users only so far. Studying the breakdown reactions by isothermal X-ray powder diffraction studies and non-isothermal thermogravimetry was done in order to test, verify and supplement interpretations delivered from other analytical techniques used. Moreover, it was tried to assess two master plot approaches offered in recent literature namely the $z(\alpha)$ master plot and the generalised time master plot method proposed by the ICTAC kinetics committee in 2011 (Vyazovkin et al. 2011). To

our knowledge, this type of master plot approach was not yet used in the Geoscience community. An integrated attempt to interpret an obvious multi-step dehydroxylation scenario on base of a thermoanalytical approach is made in comparison to contributing data from the field of vibrational spectroscopy (Trittschack et al. 2014). A summary of the suggested reaction mechanism is given in Fig. 1.

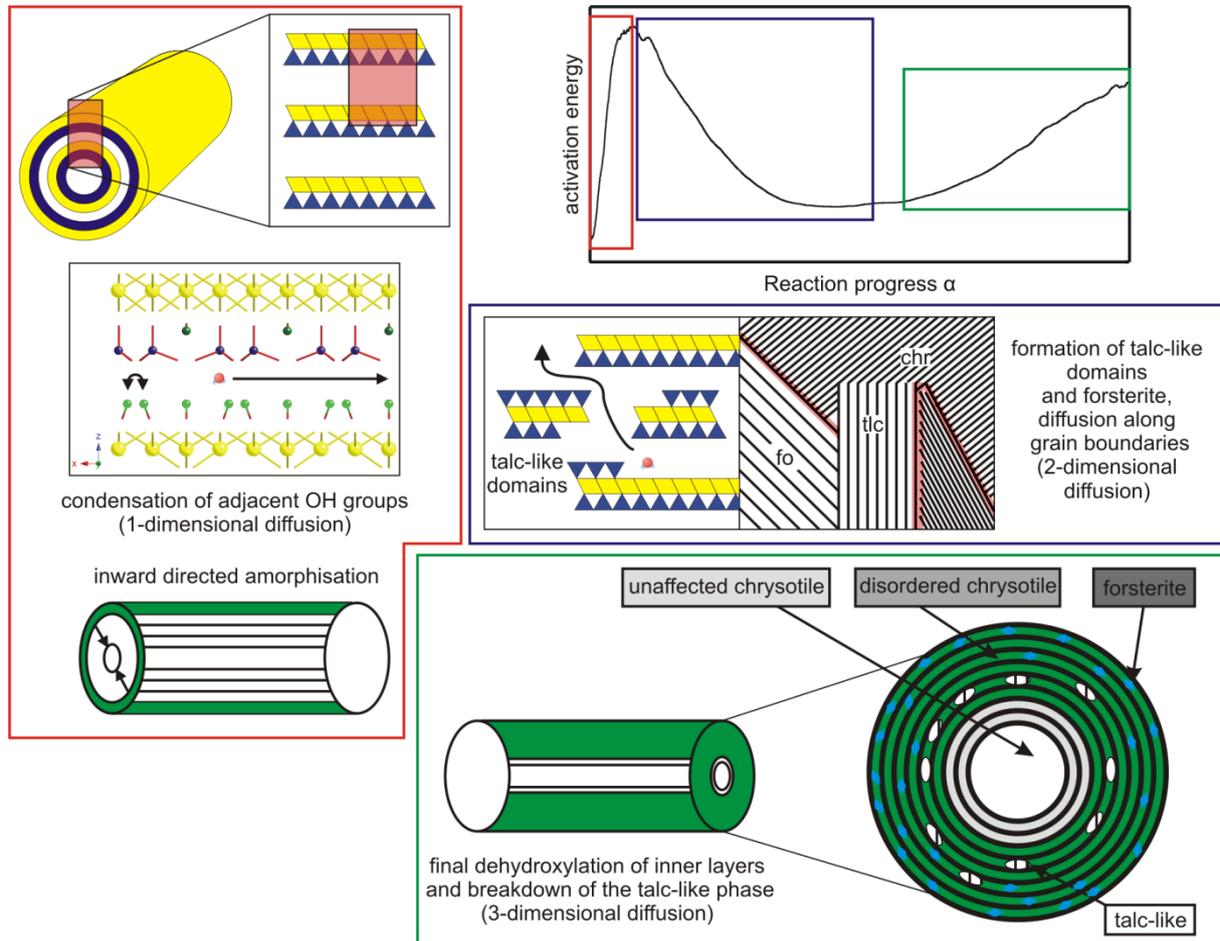


Fig. 1: Schematic sketch summarising the proposed multi-step reaction mechanism scenario of the chrysotile dehydroxylation. Colour-coded windows correspond to three different stages of the E_a versus reaction progress graph. Although they are acting simultaneously, the proposed mechanisms are interpreted as the rate-determining mechanism for the respective stage of the reaction.

References

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