

The dehydroxylation of serpentine minerals: an in situ micro-FTIR and micro-Raman spectroscopy study

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The rock-forming serpentine minerals lizardite, chrysotile and antigorite are major constituents of altered mafic and ultramafic rocks, but also have a significant contribution to the global geochemical cycle as they are a major carrier of water and mobile elements such as B, Cl, Li, As, Sb, Pb, U, Cs, Sr and Ba (Guillot and Hattori 2013). Serpentine minerals, in general, are a polymorphic group with a common chemistry of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. These phyllosilicates are build-up of a hexagonal arrangement of SiO_4 tetrahedra which are connected to $\text{Mg}(\text{O},\text{OH})_6$ octahedra by sharing the apical oxygens of the T-sheet. The misfit between both sheets is either relieved by structural or chemical modifications or a combination of both. These modifications give rise to the peculiar structures of chrysotile (nanofibres) and antigorite (corrugated) in comparison to flat lying lizardite. The latter is, thus, often characterized by an elevated amount of Al compared to the outer polymorphs (Wicks and O'Hanley 1988).

Although the dehydroxylation behaviour has been extensively studied since long by ex situ X-ray diffraction analyses, so far less has been done to examine the phase transformation reactions of serpentine minerals in situ by Raman and FTIR based techniques. X-ray diffraction studies often tried to identify a possible intermediate phase during serpentine dehydroxylation and their effect on the breakdown reaction, serpentine to forsterite and enstatite plus H_2O , itself. However, almost all of these studies proposed an intermediate phase, but amorphous in nature. Their role on the overall reaction kept a matter of debate as well as the impact of the structure on the dehydroxylation reaction (e.g., Martin 1977).

Here, we present the results of high-temperature, ambient-pressure in situ micro-Raman and micro-FTIR dehydroxylation experiments done on lizardite and chrysotile. FTIR data of the lizardite dehydroxylation point towards a temperature stability up to around 450 °C with a single dehydroxylation maximum at around 530 °C. Contrary to that, Raman data indicate a much higher dehydroxylation maximum lying at around 640 °C. Such differences mainly arise from different samples used, i.e., a transparent lizardite flake made by pressing lizardite powder in a diamond-anvil cell (FTIR) compared to some slightly pressed powder used in Raman studies. However, this differences stress the influence of the type of sample used and their arrangement within a micro-Raman and micro-FTIR compatible heating stage.

A significant change in the lizardite Raman spectra occurs between 639 °C and 665 °C. There, almost all lizardite-related modes disappear contemporaneously with the appearance of forsterite-related modes and non-forsterite related ones at 183 cm^{-1} , 350 cm^{-1} and 670 cm^{-1} . The latter three can be attributed to the presence of a talc-like intermediate without any clear evidence(s) for the presence of (a) OH mode(s). Moreover, it is possible to show a delayed breakdown of lizardite modes corresponding to the tetrahedral sheet with respect to octahedral modes.

The dehydroxylation interval of chrysotile is much broader compared to lizardite, an effect which can directly be related to the bended structure of chrysotile. The latter causes a radius-dependent dehydroxylation reaction and, thus, an inward directed phase transformation. The total dehydroxylation interval (Raman data) is between around 450 °C and around 800 °C, while this range is characterised by the co-occurrence of chrysotile, the talc-like phase and forsterite. The dehydroxylation maximum in FTIR data is situated at around 600

°C. A comparison of the relative integral intensities of a talc-like feature (band near 183 cm⁻¹), forsterite modes (ν_1 and ν_3 forsterite stretching doublet) and a lizardite feature (ν_1 Si-O_b-Si) illustrates a major intensity decrease of lizardite features at 400 °C and a first appearance of forsterite and the talc-like phase at around 450 °C. Whereas the forsterite intensity steadily increases up to the highest temperature measured (871 °C), the intensity of the talc-like phase reaches a maximum at around 720 °C. Afterwards, there is a significant decrease in the latter which lead to the complete disappearance at 871 °C. Compared with the lizardite breakdown reaction, talc-like Raman modes are situated at the same wavenumber position with one exception, namely the appearance of a talc-like OH mode at around 3677 cm⁻¹. For more details see Trittschack et al. (2012) and Trittschack and Grob ty (2013).

The outcome of this study emphasises the appearance of an OH bearing, talc-like intermediate phase during the breakdown reactions of chrysotile and lizardite. The missing OH band in lizardite data is related to the fast appearance and disappearance of talc-like features which prevent a detection of a low intensity OH band so far. Nevertheless, the appearance of an OH containing intermediate is complicating the phase transformation by adding an additional step to the reaction. This fact has to be kept in mind when dealing with the serpentine breakdown in petrological grids covering low-pressure conditions and modelling the storage and release of mobile elements important in fluid geochemistry. It is also important in the field of carbon-capture-and-storage as serpentinites are potential rocks for the long-term storage of CO₂.

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