There are two known **stable isotopes of hydrogen** in nature: protium (<sup>1</sup>H, commonly labelled just H) and deuterium (<sup>2</sup>H, commonly labelled as D). On Earth the D/H ratio varies from tens of ppm in precipitation over Antarctic to 156 ppm in oceanic water, with D/H in minerals and brines remaining within that range. In contrast, Solar wind is deuterium-free whereas some meteorites and Venus planetary atmosphere show extreme D enrichment resulting in D/H >0.01, and up to 1 in dense molecular clouds. **Hydrogen isotope fractionation** (changes in D/H ratio due to various processes) is probably the most common isotope reaction in the universe, as hydrogen is the most abundant element. Hydrogen occurring in mineral structure as a part of hydroxyl (OH) groups is responsible for fluids presence and circulation in the upper part of Earth lithosphere. In **phyllosilicate minerals** (layer-type minerals, like muscovite, biotite, kaolinite, talc, chlorite), which are one of the most abundant groups of minerals on Earth (and present also on Mars and other terrestrial planets), the OH group content is especially high; therefore, these minerals are the major vessel for fluids delivery for metamorphic and melting processes during subduction.

Hydrogen can be removed from minerals by heating, naturally or under laboratory conditions, in two major thermally-induced reactions: **dehydroxylation** and **dehydrogenation**. Dehydroxylation (the removal of OH groups) proceeds by the formation of one H<sub>2</sub>O molecule from two OH groups, leaving one hydroxyl oxygen in the mineral structure. Dehydrogenation (removal of H, not OH), does not involve hydroxyl oxygen atoms but requires the presence of Fe(II) or other common redox element in the mineral structure. Particular pathways of these two reactions, dehydroxylation and dehydrogenation, remain, however, unclear.

Partial removal of hydrogen in a form of H<sub>2</sub>O during evaporation from liquids (eg. water) causes the enrichment of the remaining (liquid) portion of water in Deuterium. Similar enrichment has been observed in minerals which were partially heated in a volcanic magma chamber or under laboratory conditions: the OH groups remaining in the structure become more and more enrich in D. However, the knowledge about these processes in minerals is poor. The scattered data and incomplete conclusions, and apparent links between diverse experiments, and implications from different, plausible mechanisms of H removal call for a systematic study on the evolution of H isotope composition during partial dehydroxylation and dehydrogenation in phyllosilicates.

## The main hypothesis that will be pursued in the project is if the probability of H isotope fractionation during thermal alteration of phyllosilicates depends on the actual mechanism of dehydrogenation and dehydroxylation.

The hypothesis will be tested using specially selected pure phyllosilicate samples of different structure and composition, which corresponds to different H removal mechanisms. The samples will be partially dehydroxylated and dehydrogenated using dedicated experiments under different conditions. The thermally treated samples will be analyzed for their structural alterations and the iron oxidation state. State-of-the-art methodology will be applied to determine the H and O isotope composition in solid samples and in the gases evolved during heating their heating under various conditions.

Results of the study will be used to understand the H isotope fractionation in minerals that occurs during their migration toward the Earth mantle. The isotopic signature of deep-seated fluids released form the phyllosilicates would be different than their shallower counterparts. If found as common reaction, H isotope fractionation in phyllosilicates during degassing would contribute to our knowledge on the H isotope budget in metamorphic and magmatic fluids.