

Methane (gas) hydrates are ice-like substances composed of solid water and methane gas. Natural gas hydrates are commonly found under the seafloor along continental margins at low temperature (ca. 0-5°C) and high pressure conditions. Hydrates are not stable at the Earth's surface, where the surrounding pressure is too low. Interestingly, they may burn and release liquid water at the same time and so they are called "*burning ice*". Yet, they can also become unstable below the sea floor. Changes of pressure/temperature conditions at the seafloor, such as ocean warming or sea-level drop, may destabilize hydrates on a global scale leading to liberation of large quantities of H<sub>2</sub>O and CH<sub>4</sub> to the sediments and ocean water. Released gas and water heavily affect physical properties of the sediments, e.g. by decreasing their density, which triggers submarine slumps. CH<sub>4</sub> may also escape to the atmosphere.

Upon decomposition, 1 m<sup>3</sup> of gas hydrate liberates even up to 180 m<sup>3</sup> of CH<sub>4</sub>. Most of the Earth's natural gas is currently stored in gas hydrates and they represent a huge and tempting potential energy resource. Technology of methane extraction from hydrates has recently been relatively well developed and several countries have already launched national projects on the exploration and exploitation of gas hydrates, including USA, Canada, India, China and Japan. Commercial hydrate exploitation seems to be just a matter of time if the demand and prices of energy continue to increase. However, industrial intervention in the hydrate-bearing submarine slopes constitutes a serious environmental and climatic risk. Extensive hydrate extraction may cause not only regional disasters, such as giant submarine slope failures, earthquakes, tsunamis, but also acceleration of global warming and ocean acidification, because CH<sub>4</sub> is a much more effective greenhouse gas than CO<sub>2</sub>. Therefore, any globally changes of hydrate stability, e.g. caused by ocean warming, may significantly influence the Earth's climate.

Since "*the past is the key to the future*", investigations of the role of gas hydrates in the past climatic and biotic perturbations can be vital for our understanding of the threats related to current climate change and potential exploitation of hydrates. Some of the most severe greenhouse conditions, such as the Paleocene-Eocene Thermal Maximum (PETM) and mass extinctions, e.g. the end-Permian extinction, are linked to massive and worldwide dissociation of gas hydrates. Unfortunately, the role of gas hydrates in the geological history is still not well-constrained, because these ephemeral substances are not preserved in the rocks. How can we, therefore, identify former presence of gas hydrates in the geological record? A very specific kind of carbonate rocks, called "*clathrites*", forms in genetic association with gas hydrates. They develop at or slightly below the seafloor through precipitation of carbonate minerals, such as aragonite, calcite or dolomite, in areas where methane is bubbling through the sediments. Former presence of gas hydrates can be, therefore, inferred from investigations of fossil clathrites. Reports of such rocks are, however, extremely rare and their recognition is clearly underestimated. Three potential reasons of this underrepresentation are hypothesized:

1. There are no clear criteria for their recognition in the rock record, where gas hydrates are not preserved.
2. Clathrites are difficult to study. Advanced methodology is necessary for their identification.
3. Much of geological mapping took place when formation of clathrites was not understood yet.

Whilst clathrites are obvious manifestations of past hydrate occurrence, slow decomposition of hydrates and less abundant carbonate precipitation may result in marly rocks with less distinctive properties. Such rocks may have been easily overlooked, also in the intervals representing greenhouse events, such as PETM, for which evidence of hydrates in sedimentary record has not been found. Therefore, it will be tested whether such marly deposits, which experienced methane seepage, carry evidence of hydrate dissociation. If so, further studies may amplify the recognition of similar hydrate-associated rocks and fill gaps in the sedimentary record of global greenhouse events.

This project will stimulate future research on fossil clathrites by defining well-constrained and comprehensive criteria for their identification and by applying and testing advanced, potentially valuable geochemical methods. It will also contribute to the understanding of the true role of gas hydrates in the Earth's history, which can allow us to better predict the potential consequences of future climate change and exploitation of hydrates. This will be achieved by careful research on relatively well-documented, ancient hydrate-associated rocks and their modern counterparts through international collaboration with research teams working on these deposits and by application of state-of-the-art and novel research methods. Ancient rock samples will come from the Carpathians, Piedmont, and Northern Apennines. They will be compared to clathrites recovered from modern sediments offshore Oregon.