Summary

Fluids are of major importance in many chemical and physical processes throughout the Earth. Research on fluid dynamics in nature is of great economic and societal relevance as it enhances our capacity to assess geohazards, the distribution of natural resources, and the potential for subsurface storage of \( \text{CO}_2 \) and nuclear waste. Among the approaches for studying fluid systems, particular attention goes to minerals that precipitated from ion-bearing fluids. Mineral precipitation takes place whenever fluids reach a state of supersaturation due to a change in temperature, pressure or fluid chemistry. Mineral deposits occur from deep sedimentary basins to the surface hydrosphere; fracture-filling veins, cave formations (speleothems), travertines and biogenic skeletons are all examples of natural mineral precipitates. The chemistry of minerals is tightly linked to their parental fluid. Since fluids themselves barely fossilize, chemical data of minerals are widely exploited to indirectly infer fluid properties. Locked up in minerals, however, there is one archive - hidden to the naked eye - that can provide direct information on paleo-fluids: fluid inclusions.

During mineral growth, minor fluid quantities typically get entrapped within imperfections in the crystal lattice. These so-called fluid inclusions represent microscopic traces of original mineral-forming fluids and hence constitute an important target for fluid provenancing studies. Multiple analytical techniques have been developed through the course of time to determine chemical and physical properties of fluid inclusions. Whereas some of them are already well-established, the potential of many more techniques is left to be discovered. The focus of this thesis is on the hydrogen and oxygen isotope record (\( \delta^2\text{H} \) and \( \delta^{18}\text{O} \)) of fluid inclusion water. This record evokes a special interest since it is directly coupled to the main constituent of mineral-forming fluids: the water molecules. Isotope signatures of water vary throughout the numerous water reservoirs on Earth due to systematic isotope fractionation processes (e.g., evaporation, precipitation, water-rock interactions) and are, therefore, a powerful tracer for fluid provenance.

Techniques for isotope analysis of fluid inclusion water are continuously evolving. The latest technical advances are moving towards continuous-flow set-ups that involve low-temperature crushing of samples and subsequent on-line analysis of both \( \delta^2\text{H} \) and \( \delta^{18}\text{O} \). This technical procedure circumvents certain limitations of traditional techniques for fluid inclusion isotope analysis, which rely on thermal decrepitation of fluid inclusions at elevated temperatures (i.e., > 400˚C). The new-style techniques have already widely proven to produce reliable data for speleothem calcites, which represent ideal sample material due to the stable environmental conditions under which they develop. Now, this raises the question as to how functional the technique is for characterizing fluids in mineralization systems that are more complex from a physico-chemical point of view.
In this thesis, the value of fluid inclusion isotope analysis is investigated when applied on i) vein minerals and ii) biogenic carbonates. Vein minerals develop in subsurface fracture networks and constitute a record of fluid migration patterns at deep crustal levels. A complicating factor in vein systems are alteration processes that may obscure primary isotope signals in fluid inclusion water (e.g., recrystallization, fluid infiltration, isotope exchange, hydrogen diffusion). Hence, fluid inclusions do not necessarily constitute black boxes for past-hydrogeological environments, which makes an adequate petrographic and geologic framework indispensable for any fluid inclusion study on vein systems. Biogenic carbonates refer to any skeletal build-up produced by organisms. From a geologic viewpoint, biogenic carbonates in the marine realm (e.g., corals, foraminifera, mollusks) are particularly interesting as they may hold geochemical proxies for past environmental conditions.

The work presented in this thesis is based on four distinct case studies that are discussed over six chapters (Figure 1). In the first chapter, the research goals and the basics behind the application of fluid inclusion isotope analysis are set forth; it also provides a detailed description of the technical procedures. Chapter 2 describes a case study on calcite veins in a carbonate platform on the passive margin of northeast Brazil. The hydrogeological system is relatively simple and consists of upwelling of meteoric water from an underlying sandstone reservoir. Fluid upwelling in the carbonate rock formation is controlled by episodes of fracturing and was most intense during the syn-subsidence evolution of the basin. In Chapter 3, a case study is presented on fluid flow in Cretaceous to Paleocene carbonates from the Ionian Zone in the Albanide fold-and-thrust belt. Fluid inclusion isotope data of calcite vein cements reveal a more complex fluid system, which involves mixing of meteoric water with saline formation fluids. Meteoric fluids are charged in the hinterland and gain in dominance through time as thrusting advances. Fluid temperatures in the Brazilian and Albanian case studies are relatively low, thereby incapacitating most conceivable post-depositional alteration processes of fluid inclusion water.

Chapter 4 presents a case study on vein mineralization in the Harz Mountains, which precipitated from high-temperature hydrothermal fluids. The strong temperature decrease that vein minerals in the Harz Mountains experienced since deposition forced oxygen isotope alteration of fluid inclusion water trapped in the oxygen-bearing minerals calcite and quartz. Despite the influence of certain alteration processes through the course of time, isotope signals in the Harz case study allowed for inferring a mixing system with marine evaporation fluids controlling the deposition of ore-bearing minerals. Altogether, fluid inclusion isotope data of vein minerals can give a unique look into subsurface fluid systems. The work presented in this thesis also reveals that oxygen isotope equilibrium could be less common in basinal fluids than commonly assumed. This may have consequences for existing methodologies for calculating oxygen isotope values of paleo-fluids that are based on the assumption of isotope equilibrium.

Chapter 5 elaborates on isotope data of fluid inclusion water incorporated in cold-water coral skeletons. Biogenic calcification in corals is highly complex and remains a topic of debate. Gaining insight into coralline biomineralization is
essential for understanding how corals will react to (anthropogenic) environmental changes. Fluid inclusion isotope data reveal that skeletal aragonite precipitates from a mix of seawater and metabolic water produced within the coral organism. An offset from the expected mixing line between the two endmembers is best explained by a fractionation step in the hydration spheres of Ca\(^{2+}\) and CO\(_{3}^{2-}\) ions. The data support biomineralization models that involve precipitation of aragonite through clumping of amorphous precursor particles in restricted volumes, rather than traditional models involving calcification from an extracellular zone at the tissue-skeleton interface. This may imply that corals are less sensitive to environmental change than commonly thought. Since fluid inclusion isotope signals are ultimately related to metabolic rates, there is potential for the isotope record to be developed into a proxy for environmental parameters and coral vitality in general.

The results of the four case studies are synthesized in Chapter 6. Altogether, this thesis demonstrates that the application of continuous-flow techniques for fluid inclusion isotope analysis could constitute a step forward in accurately determining isotope ratios of fluid inclusions in a variety of mineral types. Even vein deposits that date back to the Mesozoic and that crystallized at temperatures far above 100˚C may provide meaningful fluid inclusion isotope data. It is, thus, a data source that can be used as an important shackle in integrated geological studies on fluid dynamics in a wide range of mineralization systems, from the micro- to the macroscopic scale and dating from millions of years ago to the present.