SUMMARY

Understanding past climate variability is of key importance to better predict future climatic evolution. Models used to predict future climatic changes such as sea-level rise, temperature increase or water-column hypoxia are often tested and validated by their ability to mimic past climate variability due to changes in environmental factors and orbital configurations. As instrumental records are limited in time, geological archives such as tree rings, ice cores and sedimentary records are used. So-called proxies, obtained by the analyses of these sedimentary records, are used to reconstruct past environmental settings and climate change. Paleontological proxies such as the distribution of dinoflagellate cysts, inorganic proxies like stable isotopic compositions of foraminifera shells and organic proxies based on biomarkers represent different types of proxies. The organic ones reflect specific source organisms, their habitats and/or biochemical processes at the time of deposition. However, as these proxies have limitations they have to be studied extensively and new ones need to be developed.

In this thesis the focus is on one class of biomarkers and their potential as proxy: the long-chain diols. These compounds have a long carbon chain with two hydroxyl groups, are often resistant to degradation and can be found in sediments up to 65 million years old. They are widespread common compounds in marine and freshwater environments although their source organism(s) are not well known. In freshwater environments, eustigmatophytes, a group of unicellular phototrophic algae, are probably the main producers, while in the marine realm the sources of just a few long-chain diols are well known. The 1,14-diols are produced by *Proboscia* diatoms and *Apedinella radians,* whereas the source organisms of the other long-chain diols, i.e. 1,13- and 1,15-diols, are unknown.

The relative abundance of long-chain diols varies with sea water temperature, the C_{30} 1,15-diol being more abundant in warmer waters, while the 1,13-diols (C_{28} and C_{30}) are more abundant in colder waters. Following this observation, the Long-chain Diol Index (LDI) has been developed and a calibration curve of this proxy based on the analysis of a large number of surface sediments worldwide permitted the reconstruction of sea surface temperature (SST) in the past. However, due to the lack of knowledge of marine long-chain diol producers and their habitats, the LDI cannot be calibrated using laboratory cultures. Related to this, it is not clear how far back in time the LDI can be applied to reliably reconstruct SST. This lack of knowledge regarding the sources and the controls on long-chain diol distributions in the water column is also severely hampering their application as reliable proxies.

This thesis focuses on understanding what exactly determines long-chain diol distributions, which organism(s) are producing them in marine and freshwater environments, and how they can be reliably used as proxies to reconstruct the past. The thesis is divided into two parts: Part I focuses on long-chain

diols in modern marine and freshwater environments and Part II describes the application of long-chain diol proxies.

Part I integrates results of modern long-chain diol distributions determined in present-day settings going from the open ocean to rivers and lakes via coastal margins. In an equatorial cross Atlantic transect, long-chain diols in the water column were dominated by the C_{30} 1,15-diol, in agreement with the presence of relatively warm surface water. However, 18S rRNA analysis suggested that this and other long-chain diols were not derived from *in situ* production but from dead organic matter, severely hampering lipid/DNA comparisons and the search for their source organisms. Surprisingly, the Amazon plume, representing the western end of the transect, did not seem to impact the marine long-chain diol distributions. To investigate if other rivers and terrestrial organic matter have an effect on marine long-chain diol distributions, four coastal margins influenced by major rivers were examined. The C_{32} 1,15-diol was recognized as an important component of riverine origin. Because other long-chain diols are also partly derived from the rivers, in particular the C_{30} 1,15-diol, the LDI is not properly reflecting SST. Thus, along coastal margins impacted by riverine organic matter, the LDI is not reliable. We therefore developed a tool to assess if the sampling site is influenced by rivers using the fractional abundance of the C_{32} 1,15-diol ($F_{C32\ 1,15}$), which increases upon increasing river impact. We suggest that this new proxy can be used to trace river influence in past coastal settings (see below).

Since the sources and controls of freshwater diols are not yet well understood in river systems, we studied the Godavari, Danube and Rhine rivers. Long-chain diol concentrations were found to be enhanced in low flow areas such as lakes and side ponds. Therefore, two lakes were investigated, namely temperate Lake Geneva (Switzerland/France) and tropical Lake Chala (Kenya/Tanzania). In Lake Geneva, the long-chain diols were mainly produced from spring to late summer and their relative distributions changed over this period. Their production was enhanced during periods of thermal stratification of the water column. These results were confirmed by the four years sediment trap study of Lake Chala. 18S rRNA analysis of Suspended Particulate Matter (SPM) from Lake Geneva corroborated previous findings that eustigmatophytes produce long-chain diols in freshwater systems. Species related to *Nannochloropsis* spp. were probably responsible for the C_{32} 1,15-diol production during spring, while species related to *Ellipsoidion edaphicum* might have been responsible for the abundance of C_{30} 1,15-diol during summer, although their long-chain diol distributions have not been studied in cultures.

In part II, the new proxy developed to trace river input in shelf seas, $F_{C32\ 1,15}$, as well as other diol proxies were tested and applied to the analyses of several sedimentary cores. A comparison of the $F_{C32\ 1,15}$ with the BIT index (a proxy for river and soil input) in sedimentary cores from the Mozambique Channel, offshore the Zambezi River and in the eastern Mediterranean, offshore the Nile River, showed a close correspondence, further confirming the applicability of $F_{C32\ 1,15}$ to trace river input. Periods during which the results of the two proxies differed, corresponded to periods of changes in sources of soil input, indicating that a multi-proxy study allows for a better understanding of erosion processes.

The $F_{C32\ 1,15}$ was also applied to reconstruct the past in a long sedimentary core, covering the last 1.5 million years, from the central Sea of Okhotsk. As observed in the case of the Mozambique Channel and Mediterranean Sea, the $F_{C32\ 1,15}$ was mainly driven by changes in sea level. Its periodicity was dominated by the 100-kyr Milankovitch orbital cycle. This cycle, which is caused by changes in the eccentricity of Earth's orbit, causes changes in the global ice volume and sea levels over such timescales. The LDI temperature proxy was indicative of autumn SST during the Holocene and other interglacials whereas it seemed to reflect summer SST during glacial periods. This shift in glacial/interglacial seasonality was responsible for the lack of a strong periodicity in the LDI record. Furthermore, proxies based on the occurrence of 1,14-diols clearly indicated a periodicity of *Proboscia* diatom productivity over such timescales. The primary productivity in the Sea of Okhotsk was enhanced during deglaciations and was mainly driven by sea ice advance and retreat, as indicated by the dominant 100-kyr periodicity of the 1,14-diols record.

The results described in this thesis allowed for the development of a new diol-based proxy for river input, which, in combination with other proxies, enables a much better understanding of riverine production and transport, and of soil erosion processes. Furthermore, the limitations of previously developed long-chain diol-based proxies are now better recognized. New paleo-reconstructions in both tropical and polar regions have been generated, enabling improved reconstructions of past climatic changes and a potential to better test and validate climate models.