

5 Summary and perspectives

In this thesis, the applicability of long-chain *n*-alkanes and *n*-alkan-1-ols as biomarkers to deduce the C₄ plant contribution to the vegetation was evaluated. As a first step, the plant waxes were analysed to validate the reliability of these components as C₄ plant proxies. Furthermore, the applicability was proven in Holocene sediment samples from a North to South transect along the southwest African continental margin. This transect parallels distinctive phytogeographic zones from C₃-dominated vegetation types to C₄-prevailing vegetation. In combination with pollen analyses of the same sediments, with known phytogeographic zones and known transport ways of organic material the biomarker signatures were checked on an almost continental scale. The proven reliability was then extended to reconstruct vegetation changes in the past during climatic variations of recent glacial/interglacial changes.

C₄ grasses appear to be the most important source of C₄ biomass in the geological record. Their distribution across the world in broad latitudinal belts is governed by climatic conditions of dry and arid tropical and subtropical areas. The C₄ grass subfamilial distribution is linked to the abundance of C₄ subtypes within them, which prefer different habitats of annual rainfall patterns (Schulze et al., 1996; Taub, 2000; Wan and Sage, 2001). Grasses of the subfamily Chloridoideae or grasses containing the C₄-PCK or C₄-NAD-ME subtypes thrive in extreme arid habitats. In such areas C₃ plants act with wide open stomata to counteract photorespiration. This reduces their water use efficiency dramatically. C₄ plants have more competitive success due to an adapted physiology, the CO₂ concentrating mechanism. Generally, the C₃ versus C₄ relationship in tropical and subtropical regions simply reflects the tree versus grass contribution to the vegetation. The extension or regression of tropical grasslands and savannas may hold important regional climatic information for the palaeoclimatic orientated scientist.

For validation, waxes of 35 C₄ grasses from the southern African grasslands and savannas and of three C₃ grasses from Peru and Australia were analysed for their carbon number distribution and stable carbon isotopic composition of long-chain *n*-alkanes (*n*-C₂₇ to *n*-C₃₅) and *n*-alkanols (*n*-C₂₂ to *n*-C₃₂). The investigated subspecies were chosen according to their abundance in southern Africa. Separated plant parts (flower, leaf, stem) of two grass species exhibit different homologue patterns, but the compound-specific isotopic composition seems to be unaffected. Significant amounts of shorter-chain *n*-alkanes in flower heads may have affected the whole-plant biomarker signature. *n*-Alkanol distribution patterns exhibited no systematics. The data are too limited to draw a

general conclusion and further investigations are required. The distinctive distribution patterns in plant parts may be the reason, why a chemotaxonomic relationship on a species level of whole grass samples was not successful.

The lipid data were separated in several groups by averaging on a photosynthetic, on a C₄-subtype, and on a subfamilial level. At a preliminary state due to the limited number of samples, the C₃ grasses mainly contain the *n*-C₂₉ and *n*-C₃₁ alkanes and *n*-C₂₆ and *n*-C₂₈ alkanols. Their averaged weighted mean $\delta^{13}\text{C}$ values are -33.8‰ and -26.7‰, respectively. For comparison, waxes of angiosperm C₃ trees collected in Japan and Thailand contain mainly the *n*-C₂₉ alkane (Chikaraishi and Naraoka, 2003). They may represent the second-most important group of biomarkers in the C₃ versus C₄ estimations. Wax signatures of C₄ grasses are distinguishable from those of C₃ species by high contents of *n*-C₃₁ and *n*-C₃₃ alkanes and the abundance of the *n*-C₃₂ alkanol, which is largely absent in C₃ grasses. The dominant *n*-alkanes and *n*-alkanols in the C₄ species are each characterised by consistently heavier $\delta^{13}\text{C}$ values of circa -22‰. Especially chloridoid C₄ grasses or the species containing the NAD-ME or PCK C₄-subtype, which thrive in extreme arid habitats, exhibited a longer averaged chain length of the wax homologues. This suggested that these C₄ species are adapted to warm and dry tropical environmental conditions by higher melting points of their waxes. Averaged bibliographic data of *n*-alkanes and *n*-alkanols of grass waxes substantiated the obtained results for C₃ and C₄ grass waxes. A hierarchical cluster analysis of bibliographic and the data of this study exhibit nearly the same subfamilial separation for *n*-alkanes compared to the postulated evolutionary sequence of grass subfamilies (Clayton and Renvoize, 1986). The *n*-alkanol clusters coincide with the phylogeny of grasses (Grass Phylogeny Working Group, 2001). An evolutionary adaptive role of leaf waxes appears to be certain but requires further investigations. Overall, in terms of palaeoenvironmental studies of soils, lake and marine sediments, the distribution and isotopic characteristics of *n*-alkanes and *n*-alkanols constitute useful biomarker proxies for the C₄-dominated tropical and subtropical grasslands.

Wax lipids may be provided to ocean sediments directly from vegetation by wind- or river-transported plant detritus, by ablation, by natural and anthropogenic burning, and indirectly by deflation of dust particles from dry pans and semi-desert areas. Seasonal burning occurs in the investigation area, when savanna biomass, especially the grass layer, is turned into highly flammable material during senescence of plants in the dry season of the austral winter (e.g. Andreae et al., 1996; Barbosa et al., 1999). For palaeoclimatic studies this implies that seasonality and mode of transportation of plant material have to be considered. It has been reported that senescent grasses lose their flower heads and this affects the *n*-alkane signature of a whole plant (cf. Smith et al.,

2001). Hence, airborne organic matter originating from grasslands may be depleted in flower wax signatures. However, it is difficult to estimate the flower versus leaf biomarker ratio, which is transported to oceanic sediments. This calls for caution in palaeoclimatic assessments.

In southwestern Africa, offshore winds occurring during the austral winter season coincide in time with seasonal surface fires and dust storms abrading leaf waxes. The winds transport the generated aerosols and plant detritus to oceanic sediments. Hence, airborne particulate material derived from the western and central South African hinterland dominated by deserts, semi-deserts and savanna regions are rich in organic matter from C₄ plants.

Near-surface, marine sediments of late Holocene age at nine core sites were recovered during ODP Leg 175 and METEOR M6/6 and M20/2 cruises along the southwest African continent from the Congo Fan to the Cape Basin. They were used to evaluate the land plant signatures in marine sediments. Compound-specific isotopic signatures of long-chain *n*-alkanes and *n*-alkanols can be correlated with concentrations and distributions of pollen and spores taxa in the same sediments. Fluxes or accumulation rates of lipid and pollen data are roughly proportional to each other and reflect common continental source regions and transport processes. Higher values are seen at sites off the Congo River, at near-coastal sites and at sites situated in the path of the aerosol plumes derived from the arid and semi-arid areas.

n-Alkanes may be influenced by a contribution of petroleum hydrocarbons. The long-chain *n*-alkanols have the advantage of not being influenced. In the transect samples the ACL values of *n*-alkanes increase from 29.92 to 30.83 from North to South accompanied by a shift towards positive $\delta^{13}\text{C}$ values from -35‰ to -25‰ and towards higher percentages of C₄ plant pollen (approximately 7% to 60%). Similar trends are generally evident for the isotopic data of *n*-alkanols, but not for their ACL values. The alkanol patterns appear to be comprised of different assemblages of *n*-alkanol envelopes, corresponding to contributions from different groups of organisms (C₄, C₃, and CAM land plants and marine biota). Generally, the molecular isotope signature of sedimentary lipids is not as constantly distributed among the homologues as found for the C₄ and C₃ grasses. This implies mixtures of C₃ and C₄ (CAM) plant wax signatures and a potential contribution of aquatic organisms. C₄ plant estimates based on weighted mean $\delta^{13}\text{C}$ values for *n*-alkanes and *n*-alkanols parallel each other and those afforded by pollen counts. All show a north to south trend. Lowest values were found in the region of the Congo, because today's Congo River catchment area is dominated by tropical rain forest (mainly C₃ plants). The highest values occur off Namibia, where both temperature and aridity lead to a dominance of grasslands and savannas. The increased C₄ plant contributions is

probably related in higher contribution of grasses. Hence, the transect data of oceanic sediments broadly parallel the present-day distribution of C₃ and C₄ vegetation of the source areas of the adjacent continent.

The information archived in the Holocene transect was extended to the recent geological history by investigation of sediment samples representing two glacial (Last Glacial Maximum, MIS 2, and penultimate glacial, MIS 6a) and two interglacial stages (Holocene, MIS 1, and Eemian, MIS 5e) from the same nine sites. Changes in continental phytogeographic zones relating to warm and cold stages were reconstructed using the same approach by lipid and pollen analyses. As it can be expected from the present and glacial positions of phytogeographic zones, the carbon isotopic signature of the *n*-alkanes and *n*-alkanol shows an enrichment of ¹³C from North to South. Distinct differences were found in the patterns between glacials and interglacials. Generally, the latitudinal trends in the lipid and pollen data exhibit the same trends from North to South in all four time slices. The trends exhibit heavier δ¹³C values accompanied by longer-chain homologues and a higher C₄ pollen contribution. Glacial/interglacial changes are characterised by a shift of up to 25% to higher C₄ contribution in the northern part of the transect during glacial stages. Southward, the glacial/interglacial differences decrease and become negligible at the southernmost sites. Less Poaceae pollen and a higher contribution of C₃ pollen during glacial stages suggest a regional northward shift of the South African C₃ vegetation. It is inferred from these data that the open grass-rich vegetation on the southern African continent shifted northwards during glacial stages. Desert and semi-desert areas increased, and the winter rain vegetation occurred much further northward than during interglacial stages.

Uncertainties may occur in the interpretation of the results of the sediment data. The pollen assessments may be overestimated because C₄ plants produce more pollen than most C₃ plants. Furthermore, the taxa used for the C₄/CAM estimate contain C₃ species as well. The interpretation of lipid data neglects the contribution of CAM plants, potential contribution of aquatic organisms as well as stable carbon isotopic variations of the plant signature due to interglacial/glacial cycles in δ¹³CO₂ and *p*CO₂. Another reason may be the higher production of waxes by drought resistant C₄ and CAM plants. The potential contribution from aquatic organisms is unclear, although several studies have reported a low contribution of long-chain homologues to the investigated carbon-number range of *n*-alkanes and *n*-alkanols (e.g. Stránský et al., 1968; Davis, 1968; Blumer et al., 1971; Youngblood et al., 1971; Nishimoto, 1974b; Nichols et al., 1982; Nichols and Johns, 1985; Chikaraishi and Naraoka, 2003). In this project an endmember of molecular carbon isotopic composition of -35‰ for C₃ plants growing in a closed canopy and -20‰ for C₄ plants growing in open habitats is assumed in the assessment of C₃/C₄ plant contribution

by the source vegetation. However, a difference of 3.3‰ to more negative values were reported within the same C₃ plant species when going from open to closed canopies (Ehleringer et al., 1987; Ehleringer and Monson, 1993). Therefore, typically isotopic key data for C₃ and C₄ plants growing in a savanna or forest vegetation are fundamentally important in palaeoclimatic assessments. Subsequent investigations should elaborate the mentioned lack of knowledge about source organisms contributing *n*-alkanes and *n*-alkanols to the sediments and factors affecting the biomarker signatures. The results of this project broadly suggest that a combination of lipid biomarker distribution, compound-specific isotope proxies, and pollen data can be applied in the reconstruction of past continental phytogeographic developments.