

# Hydro- and biogeochemical investigations of lake sediments in the Kenyan Rift Valley

Sina Grewe



Dissertation zur Erlangung des akademischen Grades  
„doctor rerum naturalium“ (Dr. rer. nat.) in der Wissenschaftsdisziplin „Geochemie“

Fürstenfeldbruck, Februar 2016

This work is licensed under a Creative Commons License:  
Attribution – Noncommercial – Share Alike 4.0 International  
To view a copy of this license visit  
<http://creativecommons.org/licenses/by-nc-sa/4.0/>

Published online at the  
Institutional Repository of the University of Potsdam:  
URN [urn:nbn:de:kobv:517-opus4-98342](https://nbn-resolving.org/urn:nbn:de:kobv:517-opus4-98342)  
<http://nbn-resolving.de/urn:nbn:de:kobv:517-opus4-98342>

## Selbstständigkeitserklärung

Hiermit erkläre ich, Sina Grewe, dass ich diese Arbeit bisher weder an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Potsdam noch an einer anderen wissenschaftlichen Einrichtung zum Zweck der Promotion eingereicht habe.

Des Weiteren erkläre ich, dass ich diese Arbeit selbstständig verfasst und nur die in der Arbeit angegebenen Quellen und Hilfsmittel verwendet habe.

## Statement of authorship

I, Sina Grewe, hereby declare that I did not previously submit this thesis neither to the Faculty of Mathematics and Natural Science at the University of Potsdam nor to any other scientific institution.

I further state, that I did this thesis on my own and that I just used the sources and aids named in this work.

Fürstenfeldbruck, Februar(y) 2016

The picture on the front cover was taken during the expedition in September 2012 by myself and shows Lake Nakuru and the surrounding Lake Nakuru National Park.



## Acknowledgements

I am very grateful to Dr Jens Kallmeyer for giving me the unique opportunity to do this PhD. Without his support and guidance, the completion of this thesis would not have been possible. I would also like to thank my other supervisors Professor Dr Manfred Strecker and Dr Dirk Sachse for their scientific and technical support. The trips to Kenya were really gorgeous!

I like to thank the Deutsche Forschungsgemeinschaft (DFG) for funding this project as part of the Graduate School 1364. Furthermore, I want to thank all the other GRK PhD students for the nice time during our workshops and meetings outside of the university. Special thanks go to the coordinator of the GRK, Dr Henry Wichura, who helped with the organisation of the expeditions and who was always eager to help with bureaucratic problems.

Furthermore, I want to thank the Government of Kenya for providing the research permit. I am especially grateful for the help of Dr Annett Junginger, Axel Kitte, Dr Lydia A. Olaka and Nelson Khan who were a tremendous help during our field trips to Kenya. I also want to thank Dr Martin Trauth for providing us a helicopter during our trip in 2012 to reach the more secluded lakes in the Valley. Both expeditions were only successful, because our drivers James and Angus were extremely patient, when we were trying to get our cores.

Further thanks go to all the people at the university and the GFZ who made my time in Potsdam bearable: Franzi, Jonathan, Alex, Sven, Swenja, Patte, Rishi, Steffi, Bernd, Iris, Clemens, and Mashal. Thanks for your support, fruitful discussions, a nice time in the office, lab and during our badminton hours. I also want to thank Anke Kaminsky from the GFZ for giving me the opportunity to save some time in the lab. Finally, I want to thank everybody whom I forgot and who still deserves a 'thank you'.

Last, but not least, I want to thank my whole family for giving me the opportunity to recharge my batteries during my holidays which were often too short. I also want to thank Micha for always being there for me, as moral support, soundboard, and punchbag.

# Contents

<b>Zusammenfassung</b> .....	1
<b>Abstract</b> .....	3
<b>Chapter 1: Introduction</b> .....	5
<b>1.1. General information about Kenya</b> .....	7
<b>1.2 The Kenyan Rift Valley</b> .....	8
1.2.A. Evolution .....	9
1.2.B. Climate and drainage system .....	11
<b>1.3. Motivation for this thesis</b> .....	14
<b>1.4. Lakes in the study area</b> .....	15
1.4.A. Lakes in the Suguta Valley .....	15
1.4.B. Lakes in the Baringo-Bogoria Basin .....	16
1.4.C. Lakes in the Naivasha Basin .....	18
1.4.D. Former studies on the lakes .....	21
<b>Chapter 2: Materials and methods</b> .....	23
<b>2.1. Coring and sampling</b> .....	25
<b>2.2. Lake and porewater analysis</b> .....	26
2.2.A. Ion composition of the porewater .....	26
2.2.B. Hydrogen sulphide in the porewater .....	28
<b>2.3. Dissimilatory sulphate reduction</b> .....	29
2.3.A. Total reduced inorganic sulphur .....	29
2.3.B. Sulphate reduction rates .....	29
<b>2.4. Organic geochemistry</b> .....	30
2.4.A. Accelerated solvent extraction (ASE) .....	30
2.4.B. Solid phase extraction (SPE) .....	31
2.4.C. Gas chromatography/mass spectrometry (GC/MS) .....	31
<b>2.5. Overview of available data</b> .....	32

## **Chapter 3: Results and general characterisation of the lake**

<b>sediments</b>	33
<b>3.1. Introduction</b>	35
3.1.A. Ion composition of Kenyan lakes	35
3.1.B. The sulphur cycle	35
3.1.C. Origin and assignment of biomarkers	36
<b>3.2. Lake Logipi</b>	39
3.2.A. Results	39
3.2.B. Key characteristics	39
<b>3.3. Lake Eight</b>	41
3.3.A. Results	41
3.3.B. Key characteristics	43
<b>3.4. Lake Baringo</b>	43
3.4.A. Results	43
3.4.B. Key characteristics	46
<b>3.5. Lake Bogoria</b>	47
3.5.A. Results	47
3.5.B. Key characteristics	50
<b>3.6. Lake Naivasha</b>	52
3.6.A. Results	52
3.6.B. Key characteristics	56
<b>3.7. Lake Oloiden</b>	58
3.7.A. Results	58
3.7.B. Key characteristics	61
<b>3.8. Lake Sonachi</b>	64
3.8.A. Results	64
3.8.B. Key characteristics	66
<b>Chapter 4: Comparison of the lake sediments</b>	69
<b>4.1. General comparison of the lakes</b>	71
4.1.A. Water characteristics and sulphate reduction	71
4.1.B. Organic geochemistry	73
4.1.C. Biomarker composition of saline and freshwater lakes	79

<b>4.2. Degradation and transformation of organic matter</b>	79
4.2.A. Degradation of n-fatty acids	80
4.2.B. Degradation of hopanoids	81
4.2.C. Degradation of sterols	83
4.2.D. Degradation of carotenoids	85
4.2.E. Influence of lake-water chemistry on the degradation of organic matter	87
<b>4.3. The lakes as climate archives</b>	88
4.3.A. Horizons of elemental sulphur as markers for low lake levels?	88
4.3.B. Changes in the distributions of straight-chain compounds as indicators for hydroclimate?	88
4.3.C. Climate versus diagenesis	90
<b>Chapter 5: Summary, conclusions, and outlook</b>	91
<b>5.1. Summary</b>	93
<b>5.2. Conclusions</b>	95
<b>5.3. Outlook</b>	96
<b>Appendix</b>	97
Appendix I: Chemical formulas	99
Appendix II: Abbreviations	99
Appendix III: List of figures	100
Appendix IV: List of tables	101
Appendix V: Origin of photos and figures	101
Appendix VI: References	102







## Zusammenfassung

Die Seen im kenianischen Riftsystem bieten die einmalige Gelegenheit eine große Bandbreite an hydrochemischen Umweltbedingungen zu studieren, die von Süßwasserseen bis hin zu hochsalinen und alkalinen Seen reichen. Da wenig über die hydro- und biogeochemischen Bedingungen in den darunterliegenden Seesedimenten bekannt ist, war es das Ziel dieser Arbeit, bereits existierende Datensätze mit Daten aus Porenwasser- und Biomarker-Analysen zu erweitern. Für diese neuen Datensätze wurden auf zwei Feldkampagnen in 2012 und 2013 Sedimentkerne aus den folgenden Seen gezogen (von Norden nach Süden): Logipi, Eight, Baringo, Bogoria, Naivasha, Oloiden und Sonachi. Die Porenwasseranalyse wurde genutzt, um die Ionenzusammensetzungen und die Konzentrationen von Schwefelwasserstoff im Wasser zu bestimmen. Desweiteren wurden im Sediment die Konzentrationen von reduzierten Schwefelkomponenten und Biomarkern bestimmt sowie Sulfatreduktionsraten berechnet. Mit den neuen Daten wurden die Sedimente charakterisiert, die Entwicklung der einzelnen Seen rekonstruiert sowie der anthropogene und mikrobielle Einfluss auf die Chemie der Seen erforscht. Zusätzlich wurde der Einfluss der Wasserchemie auf den Abbau und die Erhaltung von organischem Material im Sediment untersucht.

Die Porenwasseranalyse zeigte, dass  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  und  $\text{SO}_4^{2-}$  die häufigsten Ionen im Porenwasser der Seen waren. Allerdings wurden die nachweislich hohen  $\text{HCO}_3^-$ -Konzentrationen in kenianischen Gewässern in dieser Studie nicht berücksichtigt. Die meisten Ionenprofile in den Sedimenten zeigen ähnliche Trends mit konstanten oder mit der Tiefe zunehmenden Ionenkonzentrationen. In den Seen selbst sind die einzelnen Ionenkonzentrationen meist niedriger. Die interessanteste Ausnahme waren die Ionenprofile von Naivasha, die einen ausgeprägten Zickzack-Trend zeigten. Dieser ist wahrscheinlich auf eine unregulierte Wasserentnahme durch ansässige Landwirte und die lokale Bevölkerung zurückzuführen.

Die wichtigsten Biomarker in den Sedimenten waren *n*-Alkane, *n*-Alkanole, *n*-Fettsäuren, Hopanoide und Steroide. Die Gesamtkonzentration an Biomarkern war in Naivasha und den Nachbarseen deutlich höher als in Baringo und Bogoria, weil dort der Eintrag an organischem Material durch den intensiven anthropogenen Einfluss (hauptsächlich Blumenanbau) höher ist. Die Verteilungen von *n*-Alkanen, *n*-Alkanolen und *n*-Fettsäuren wurden von langkettigen Komponenten (*n*-C<sub>23</sub> bis *n*-C<sub>35</sub>) und ein oder zwei kurzkettigen Komponenten sowie von ungeradzahigen *n*-Alkanen und geradzahigen *n*-Alkanolen und *n*-Fettsäuren dominiert. Diese Verteilungsmuster sind charakteristisch für junge und undegradierete Seesedimente. Abweichungen von diesem Verteilungsmuster gab es bei den *n*-Fettsäuren in Oloiden und Sonachi, wo ähnlich große Mengen an geradzahigen und ungeradzahigen *n*-Fettsäuren gefunden wurden. Letztere sind wahrscheinlich auf mikrobielle Aktivitäten im Sediment zurückzuführen. Die Biomarker-Zusammensetzung in den untersuchten Seen war ähnlich; allerdings gab es wichtige und interessante Unterschiede. In den salinen Seen, zum Beispiel, wurde eine fast komplett gesättigte Version von  $\beta$ -Carotin gefunden. Dieses Molekül stammt wahrscheinlich von Cyano-

bakterien, die in den salinen Seen vorkommen. Andere Biomarker, die nur in den salinen Seen gefunden wurden, waren drei kurzkettige *n*-Alkanole (*n*-C<sub>15</sub>, *n*-C<sub>17</sub> und *n*-C<sub>19</sub>) und zwei Sterene. Stigmasterol wurde nur in den beiden Süßwasserseen Baringo und Naivasha gefunden und stammt wahrscheinlich von Süßwasseralgen.

Bogoria und Sonachi sind für Umweltrekonstruktionen mit Biomarkern besonders geeignet, da die permanenten anoxischen Bedingungen am Seegrund den Abbau von Biomarkern verlangsamen. Besonders im Sediment von Bogoria korrelieren eine große Anzahl von Biomarkern mit Seespiegelschwankungen, wie zum Beispiel langkettige *n*-Alkane und Isomere eines fast komplett gesättigten  $\beta$ -Carotins. Die anderen untersuchten Seen eignen sich jedoch weniger gut für Umweltrekonstruktionen. In Naivasha, zum Beispiel, wird die Biomarker-Verteilung im Sediment durch den Anbau von Schnittblumen im Umfeld des Sees überprägt. Nichtsdestotrotz sind der Beginn des Blumenanbaus und sein zunehmender Einfluss auf den See, in Form von exponentiell ansteigenden Konzentrationen charakteristischer Biomarker, im Sediment aufgezeichnet. Zu diesen Biomarkern gehören langkettige *n*-Alkane, *n*-Alkanole und *n*-Fettsäuren sowie Phytosterole, Carboxylester und das *n*-C<sub>17</sub>-Alkan. All diese Komponenten sind charakteristisch für höhere Pflanzen und Algen. In Baringo führen Überweidung und Entwaldung im Einzugsgebiet zu einer erhöhten Erosion und einem damit verbundenen erhöhten Sedimenteintrag in den See. Dieser führte zu einer starken Verdünnung des organischen Materials, was eine zuverlässige Interpretation der Daten erschwerte. Obwohl einzelne Umweltrekonstruktionen schwierig waren, konnten charakteristische Horizonte in den Sedimenten gefunden werden, die sich als temporale Marker einsetzen lassen. Der auffälligste dieser Horizonte war ein Horizont, der große Mengen an elementarem Schwefel enthielt. Dieser in den Sedimentkernen von Logipi, Eight, Bogoria und Sonachi gefundene Horizont wurde wahrscheinlich zu einer Zeit abgelagert, als sehr niedrige Wasserpegel vorherrschten und somit auf den Seegründen anoxygene Photosynthese oder Sulfidoxidation stattfinden konnte.

Während Salinität und Alkalinität die Sättigungsgeschwindigkeit einzelner Biomarker nicht zu beeinflussen scheinen (*n*-Fettsäuren, Sterole, Carotinoide), scheinen sie sich auf die Transformationsgeschwindigkeit von Hopenen im Sediment auszuwirken. In den beiden Süßwasserseen Baringo und Naivasha wurde mit (Hop-17(21)-en) ein diagenetisch stabileres Hopenisomer gefunden als in den salinen Seen, in denen Hop-21(22)-en das stabilste Isomer war. Schlussfolgernd scheint die hohe Salinität und/oder Alkalinität in Bogoria, Oloiden und Sonachi die Transformation von Hop-22(29)-en zu stabileren Isomeren zu beeinträchtigen.

Im Verlauf dieser Studie hat sich gezeigt, dass Bogoria und Sonachi das größte Potenzial für Umweltrekonstruktionen basierend auf Biomarkern haben, was auf ihre permanente Stratifizierung zurückzuführen ist. Daher sollten sich zukünftige Studien an ostafrikanischen Riftseen in dieser Hinsicht auf andere stratifizierte Seen konzentrieren. In Naivasha wurden Umweltsignale durch anthropogene Aktivitäten, insbesondere durch die Blumenzucht, beeinflusst. Trotzdem ließen sich gewisse temporale Marker, wie Schwefelhorizonte, in allen Seen finden.

## Abstract

The lakes in the Kenyan Rift Valley offer the unique opportunity to study a wide range of hydrochemical environments with freshwater lakes on the one hand and highly saline and alkaline lakes on the other. Because little is known about the hydro- and biogeochemical conditions in the underlying lake sediments, the aim of this study was to extend the already existing data sets for seven of those lakes with data from porewater and biomarker analyses. With the intention of assembling the new data sets, sediment cores from Lakes Logipi and Eight in the Suguta Valley, Lakes Baringo and Bogoria in the central rift, as well as Lakes Naivasha, Oloiden, and Sonachi on the Kenyan Dome were taken during two field campaigns in 2012 and 2013. The porewater of the sediment cores was analysed for their ion compositions and hydrogen sulphide concentrations. Additionally, the concentrations of reduced inorganic sulphur species and different biomarkers as well as sulphate reduction rates in the sediment were determined. The obtained data were used to get a general characterisation of the lake sediments, to reconstruct the evolution of the single lakes, and to examine the anthropogenic and microbial influence on the lake chemistry. In addition, the influence of the lake chemistry on the degradation and preservation of organic matter in the sediment column was investigated.

Porewater analysis revealed that  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{SO}_4^{2-}$  were the most abundant ions in the lakes' porewater. However, it has to be mentioned that  $\text{HCO}_3^-$  concentrations, which are known to be high in Kenyan water, were not determined in this study. Most ion profiles showed similar trends with constant or downward increasing concentrations in the core and lower concentrations in the lake water. The most interesting exception were the ion profiles of Lake Naivasha, which showed a pronounced zigzag trend which is probably related to unregulated water extraction by farmers and the local population.

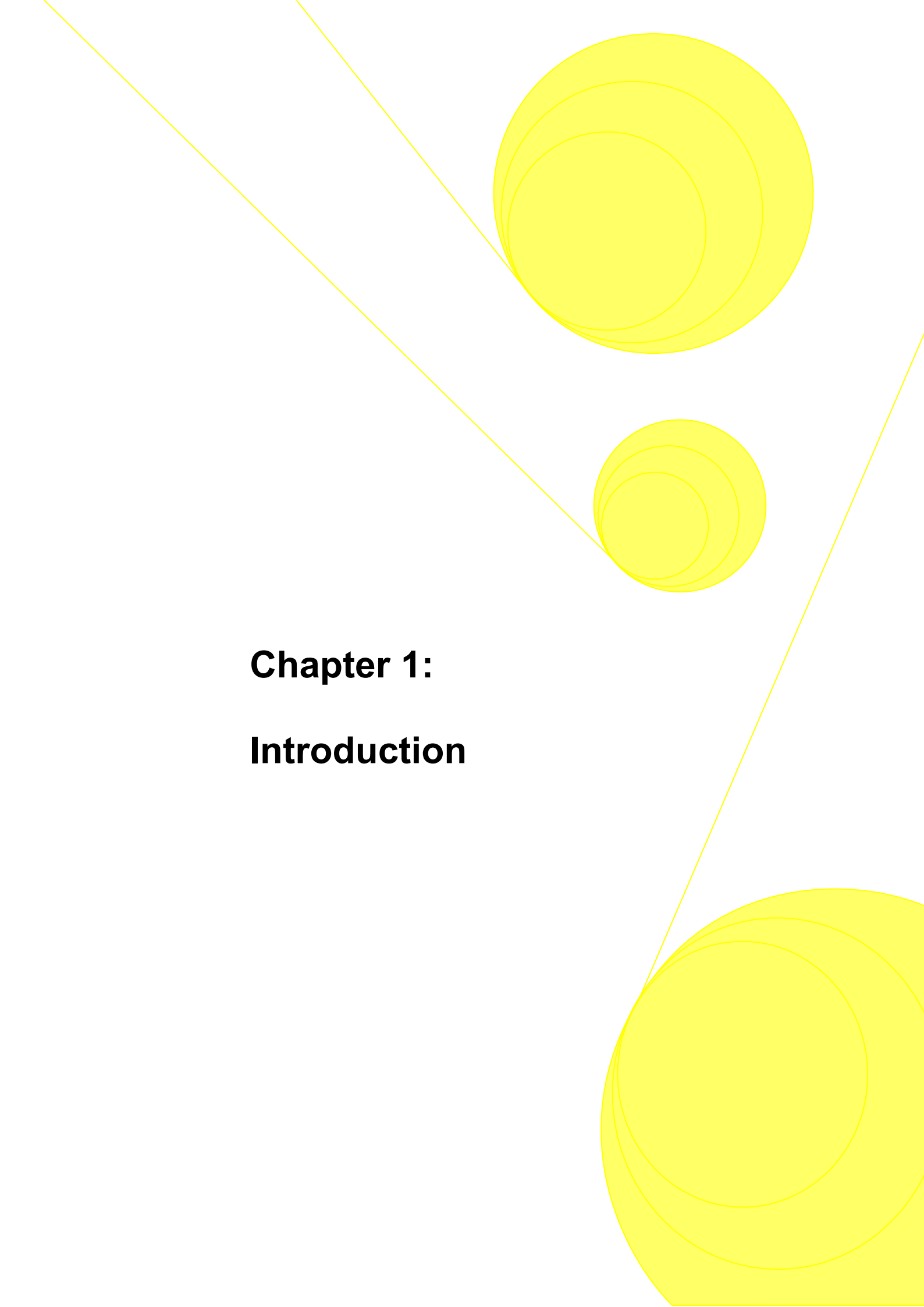
The most important biomarkers detected in the lake sediments were *n*-alkanes, *n*-alkanols, *n*-fatty acids, hopanoids, and steroids. The total biomarker concentrations were much lower in Lakes Baringo and Bogoria than in Lake Naivasha and its satellites, because organic matter input into the latter is higher due to an intensive anthropogenic influence (especially floriculture). The distribution patterns of *n*-alkanes, *n*-alkanols, and *n*-fatty acids were dominated by long-chain compounds ranging from *n*-C<sub>23</sub> to *n*-C<sub>35</sub> and one or two short-chain compounds. These distributions were dominated by odd-numbered *n*-alkanes and even-numbered *n*-alkanols and *n*-fatty acids, respectively. This distribution patterns are characteristic for fresh and undegraded lake sediments. Deviations from those distribution patterns were observed for the *n*-fatty acids of Lakes Oloiden and Sonachi, where equal amounts of even- and odd-numbered *n*-fatty acids were detected. The odd-numbered homologues are likely associated with microbial reworking. The biomarker compositions of the studied lakes were similar, although some important and interesting differences were evident. For example, the almost completely saturated homologues of  $\beta$ -carotene were detected in the saline lakes which likely originate from cyanobacteria populating those lakes. Other biomarkers restricted to the saline lakes were three short-chain *n*-

alkanols (i.e. *n*-C<sub>15</sub>, *n*-C<sub>17</sub>, *n*-C<sub>19</sub>) and two sterenes. Stigmasterol, which was only found in the two freshwater Lakes Baringo and Naivasha, likely has its origin in freshwater algae.

The degradation of biomarkers in Lakes Bogoria and Sonachi is slowed due to permanent anoxic conditions at the lake bottoms which makes those two lakes the most useful to conduct biomarker-based environmental reconstructions. Especially in Lake Bogoria, a large number of biomarkers correlated with lake level changes, for example long-chain *n*-alkanes and isomers of an almost completely saturated  $\beta$ -carotene. The other lakes of this study are less suited for environmental reconstructions. The biomarker distribution in the sediment of Lake Naivasha, for example, is overprinted by the floricultural activity around the lake. Nevertheless, the beginning of floriculture and its increasing influence with time is recorded in the sediment in form of exponentially increasing concentrations of long-chain compounds, phytosterols, carboxylate esters, and the *n*-C<sub>17</sub> alkane. All those compounds are characteristic for higher plants or algae, which multiplied due to higher inputs of fertilisers. In Lake Baringo, the high sediment input due to erosion caused by overgrazing in the catchment led to a strong dilution of the organic matter, which made it very difficult to interpret the results. Although environmental reconstructions were difficult, some lake sediments possessed characteristic horizons which can be used as temporal markers. The most prominent of those markers were horizons of elemental sulphur in Lakes Logipi, Eight, Bogoria, and Sonachi, which are likely remnants of very low lake levels when anoxygenic photosynthesis or sulphide oxidation occurred at the lake bottoms.

While salinity and alkalinity do not seem to have an effect on the saturation of biomarkers (i.e. *n*-fatty acids, sterols, and carotenoids), they do seem to affect the transformation of hopenes in the sediment. In the freshwater Lakes Baringo and Naivasha, the diagenetically more advanced hop-17(21)-ene was detected which was not detected in the saline lakes. Consequently, the transformation of hop-22(29)-ene into more stable isomers might be slowed by the high salinity and/or alkalinity in Lakes Bogoria, Oloiden, and Sonachi.

During the course of this study, it became evident that Lakes Bogoria and Sonachi have the largest potential to be used for environmental reconstructions based on biomarkers because of their permanent stratification. Consequently, future biomarker studies on East African rift lakes should concentrate on other permanently stratified lakes. Lake Naivasha is strongly influenced by anthropogenic activities, especially floriculture, which overprinted other environmental signals. Nevertheless, certain temporal markers, like the elemental sulphur horizons, were found in all lakes.

The background features three sets of overlapping yellow circles of varying sizes, positioned in the top right, middle right, and bottom right. Two thin yellow lines originate from the top left and extend diagonally across the page, one passing through the top-right circles and the other passing through the middle-right circles.

# **Chapter 1:**

## **Introduction**





## 1.1. General information about Kenya

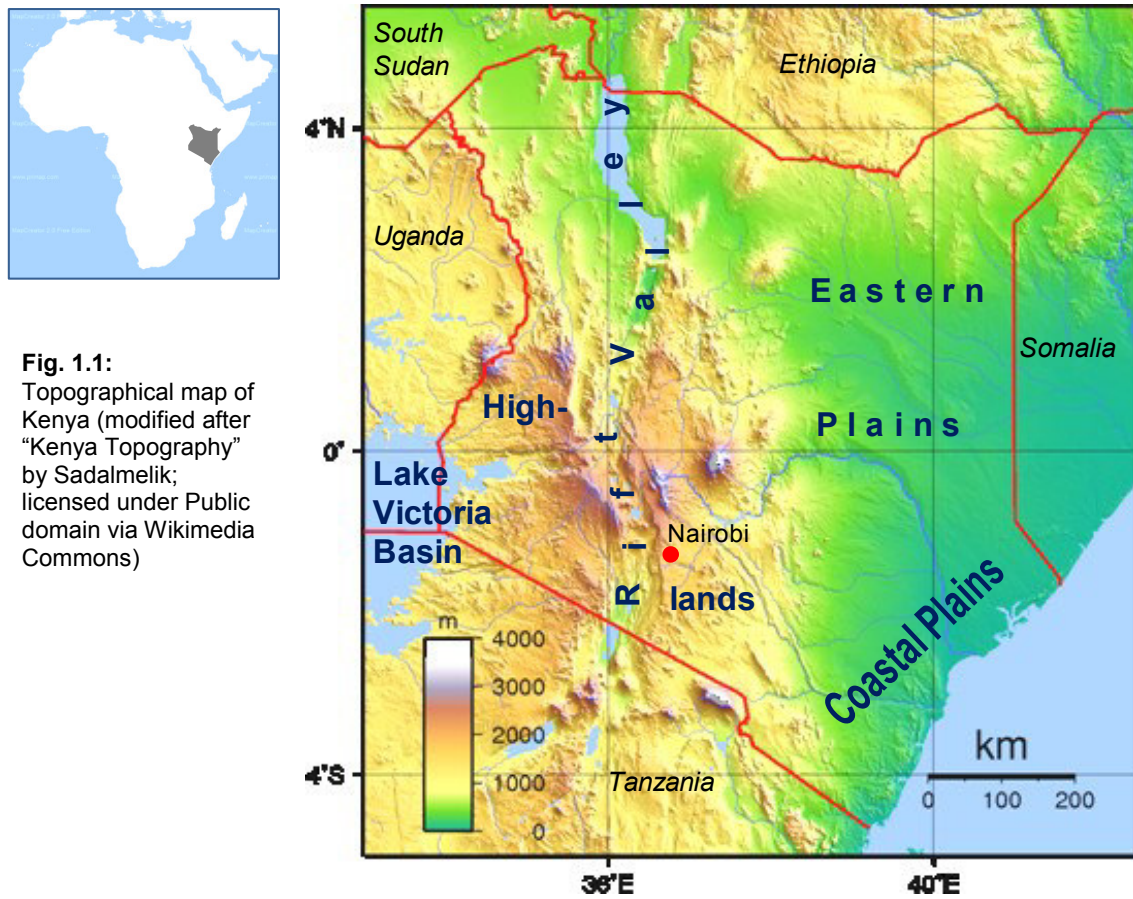
Kenya is an East African country between latitudes 5°N and 5°S as well as longitudes 34° and 42°E (fig. 1.1). It neighbours Somalia to the east, Ethiopia to the north, South Sudan to the northwest, Uganda to the west, and Tanzania to the south. To the southeast, the country also borders on the Indian Ocean. Kenya covers an area of 580 367 km<sup>2</sup> with a population of around 45 million people (July 2014, estimated; *The World Factbook* (WFB)).

Kenya can be divided into the following major relief zones: the Coastal and Eastern plains, the Central and Western Highlands, divided by the Kenyan Rift Valley, and the Lake-Victoria Basin (Mathu and Davies, 1996; fig. 1.1). Those zones show a variety of different landscapes, which are all characteristic for the African continent: huge savannahs with scattered woodlands and forests at the coast and in central and south Kenya, snow-covered peaks on Mount Kenya, desert in the north and northeast, and rain forest in the Lake-Victoria Basin (Edwards, 1940; Mathu and Davies, 1996; Brink et al., 2013).

Climate in East Africa is influenced by the passage of the Intertropical Convergence Zone (ITCZ), causing a bimodal distribution of rainfall in Kenya with 'long rains' during March to May and 'short rains' in October and November (*Kenya Meteorological Department*). The intensity of the bimodal distribution and the amount of precipitation varies, depending on the region (Brink et al., 2013; see also climate diagrams in fig. 1.2). To the west of the Kenyan Rift Valley, the most important factor influencing the climate are air circulations from the Congo Basin (Nicholson, 1996). Temperatures remain high during times of heavy rainfall (see climate diagrams in fig. 1.2). At the coast, climate is tropical and gets more temperate towards the inland (WFB). In the northern and north-eastern parts of the country, the climate is semi-arid to arid (Edwards, 1940; Mathu and Davies, 1996).

Because 80 % of Kenya falls within those arid to semi-arid lands (Mathu and Davies, 1996; Brink et al., 2013), water coverage is low (11 227 km<sup>2</sup>  $\cong$  1.9 % of total land area, WFB). The drainage system is formed by lakes (64 according to Singh et al., 2006) and rivers (mainly seasonal). The most important rivers are Tana, Athi-Galana, Ewaso Ngi'ro, and Kerio Rivers. The largest lake in Kenya is Lake Turkana in the northern Rift Valley.

Kenya is the biggest and most advanced economy in East and Central Africa (WFB). And although 75 % of the Kenyans work in the agricultural sector, merely 10 % of the country is arable (WFB). In the fertile highlands, maize, sisal, pyrethrum (an important constituent of insecticides), coffee, tea, and flowers are grown (*Library of Congress*). The large production of tea and flowers has a significant influence on the lakes in the study area. Kenya exported 494 400 t of tea (*Tea Board of Kenya*) and 124 858 t of flowers (*Kenya Flower Council*) in 2013.



**Fig. 1.1:**  
Topographical map of Kenya (modified after "Kenya Topography" by Sadalmelik; licensed under Public domain via Wikimedia Commons)

## 1.2. The Kenyan Rift Valley

Extending from the Afar Triangle in the north to Mozambique in the south, the East African Rift System is the largest seismically active rift system on Earth (Chorowicz, 2005). It extends over 6 000 km cutting through Ethiopia, Kenya, Uganda, Rwanda, Burundi, Zambia, Tanzania, Malawi, and Mozambique. A number of dormant and active volcanoes are located in and close to the rift, for example Mount Kilimanjaro (Tanzania, dormant), Mount Longonot (Kenya, dormant), and Mount Karisimbi (Rwanda/Democratic Republic of Congo, dormant) as well as Erta Ale (Ethiopia, active), Nyiragongo (Democratic Republic of Congo, active), and Ol Doinyo Lengai (Tanzania, active; [www.volcanodiscovery.com](http://www.volcanodiscovery.com)). The latter is the only active natrocarbonatite volcano in the world.

The East African Rift System consists of two main branches: the Eastern Rift Valley with the Main Ethiopian Rift and the Kenyan Rift Valley, and the Western Rift Valley with the Albertine and the Malawi Rifts (Chorowicz, 2005). The two branches encompass Lake Victoria. In the Western Rift Valley some of the highest mountains (e.g. Ruwenzori Range, up to 5 109 m) and deepest lakes (e.g. Lake Tanganyika, up to 1 470 m) of Africa can be found (Bauer et al., 2010). The lakes in the Eastern Rift Valley, on the other hand, are small and shallow, having high mineral concentrations due to missing outlets, high evaporation, and hydrothermal activities

(e.g. Tarits et al., 2006; Olaka et al., 2010). The Eastern Rift Valley is seismically less active than the western branch, but shows higher volcanic activity (Neukirchen, 2004).

In Kenya, the rift valley extends from the Turkana-Omo Low in the north to the Magadi Basin in the south. The width of the valley varies between 50 – 60 km in the Naivasha-Nakuru region (Mathu and Davies, 1996) and more than 300 km in the Turkana-Omo Low and the Magadi Basin, but it is generally less than 100 km wide (Olaka et al., 2010). With the exception of the Turkana-Omo Low, the Kenyan Rift Valley is bordered on both sides by high rift flanks (Olaka et al., 2010). The highest part of the rift valley is located between Lakes Naivasha and Nakuru on the Kenyan Dome with 2 000 m above sea level (a.s.l.). In northern and southern direction, the altitude of the rift floor is decreasing to 1 050 m.a.s.l. in the Baringo-Bogoria Basin and 250 m.a.s.l. in the Turkana-Omo Low towards the north, and 600 m.a.s.l. in the Magadi Basin towards the south. The Kenyan Rift Valley is an asymmetric half-graben (Hackman et al., 1990), which trends NNE-SSW in its central part and bends to N-S in the region of southern Lake Turkana. Between the area of Lakes Nakuru and Naivasha, the rift strikes NNW-SSE and south of it resumes the NNE-SSW trend of the central part (fig.1.1; Hackman et al., 1990). The valley is separated from the surrounding plateaus and escarpments by normal faults (Mathu and Davies, 1996), which cause displacements of up to 2 000 m in the central part (Baker and Wohlenberg, 1971).

### 1.2.A. Evolution

The East African Rift System is an early state divergent plate boundary, where the African Plate is dividing into two tectonic plates: the Somali Plate in the east and the Nubian Plate in the west (Fernandes et al., 2004). Currently, those two plates are separating with an increasing velocity from 1.9 mm/a at their triple junction with Antarctica to 6.9 mm/a at the Afar Triangle (Fernandes et al., 2004). Usually, those processes of rifting are explained by using models for ocean bottom tectonics, where disruption and separation of the crust leads to the formation of mid-oceanic ridges. But continental rifting, as it happens in East Africa, cannot be explained by those standard processes (Logatchev et al., 1972; Smith, 1994). Instead, it is assumed that heating and doming of the East African crust were the origin of the East African Rift System (Logatchev et al., 1972; Smith, 1994). Doming started around 20 Ma years ago in the area around Lake Naivasha, whereas rifting started 8 Ma later. According to Smith (1994), there were three regions of volcanic activity in Kenya:

- 1) Turkana, where tholeiitic basalts and rhyolites were erupted between 35 – 22 Ma,
- 2) the Kenyan-Ugandan border, where volcanism was strongly alkaline and carbonatitic and lasted from 31 – 22 Ma, and
- 3) the region between southern Lake Turkana and northern Tanzania, which is characterised by the eruption of weakly alkaline to transitional basalts, phonolites, and trachytes.

The following summary of the Kenyan Rift Valley's evolution is mainly taken from Baker and Wohlenberg (1971) as well as Logatchev et al. (1972). Additional sources are mentioned in the text.

**Stage 1 (23 – 16 Ma, Lower to Middle Miocene)**

The whole evolution started with the subsidence of the Turkana Depression and an uplift of the region around the Kenyan-Ugandan border. Basalts, mugearites, and rhyolites filled the Turkana Depression through massive fissure eruptions. Central volcanism with an alkaline-carbonatite composition characterised the uplifted region around the border.

**Stage 2 (13.5 – 12 Ma, Upper Miocene)**

During that time period, tectonic activity increased sharply, triggering events which pre-determined the location and evolution of the Kenyan Rift Valley. The volcanic activity shifted from the Turkana Depression southward to the uplifting Kenyan Dome and lost its connections to the Ethiopian volcanic area. The Kenyan Dome was estimated to be roughly 1 000 km in diameter and uplift was supposed to be 300 m. The Upper Miocene showed the highest magmatic productivity during the whole evolution history of rift development with large fissure eruptions of phonolites and phonolitic trachytes of about 25 000 – 30 000 km<sup>3</sup>. A huge symmetrical phonolitic shield with a thickness of 1 000 m was formed during that time.

**Stage 3 (10 – 5 Ma, Lower to Middle Pliocene)**

The third stage was characterised by southward extending volcanic activity with fissure eruptions and volcanoes in and near the developing rift. Volcanism got more central. In the western and southern regions, the petrochemical composition of the volcanic rocks remained alkaline, whereas in the eastern areas they were phonolitic and trachytic in composition. About 7 – 8 Ma years ago, phonolitic volcanism started in the south (Smith, 1994). During the climax of the Kenyan Dome uplift, first extensive rift faults developed. Those vertical fault displacements occurred mainly on the western side of the rift, whereas the eastern part showed no noticeable displacements. Even though the rift had well-defined faulted margins by ca. 10.5 Ma (Pickford, 1994), the Kenyan Rift Valley was still not defined as a real rift.

**Stage 4 (5 – 2 Ma, Upper Pliocene to Lower Pleistocene)**

After the first rifting movements, massive basalt fissure eruptions with associated minor trachytes formed a continuous horizon on almost the whole rift valley floor. In the south, eruptions were mainly caused by a group of shield volcanoes. Locally, sediments were accumulated on the basalts. Concurrently with the basalt eruptions, the large volcanoes of Mounts Kenya, Kilimanjaro, and, probably, Kulal were formed by autonomous melting centres lying east of the rift. In the area around Naivasha, massive eruptions of trachytic ignimbrites filled the rift valley in Late Pliocene. At roughly the same time, the main uplift of the Kenyan Dome and its surrounding plateaus by 1 400 m initiated the first phase of graben faulting.

During that faulting process the connection with the Ethiopian Dome was re-established. In the west, volcanic activity stopped completely with the start of rift-faulting, whereas it was then concentrated inside and east of the rift valley.

#### **Stage 5 (2 - 0.7 Ma, Middle to Upper Pleistocene)**

During that stage, spreading of the volcanic activity decreased, but the rift, especially the southern part, was still dominated by fissure eruptions. North of Mount Suswa (located south of Lake Naivasha), thick beds of ignimbrites and tuffs can be found on the rift floor and on the rift shoulders. Trachytes were probably erupted by some volcanoes north of Lake Baringo. Intensive fracturing led to the deepening of the rift valley.

#### **Stage 6 (0.7 – 0 Ma, Upper Pleistocene to present)**

In the last stage, magmatic activity migrated eastward with new volcanic centres developing east of the main eruptive centres causing partial or total extinction of those. Those new centres formed large basalt ridges. While Mounts Kenya, Kilimanjaro, and Kulal reduced their activity, fissure eruptions on the rift floor stopped completely and volcanic activity disintegrated into several separate areas of central volcanoes. That new central volcanism on the rift floor showed a higher diversity in petrochemistry, but was still strongly alkaline-carbonatitic. Faulting continued and produced small, elongated rift basins with lengths of between 30 – 50 km and length/width ratios of 4 - 5 (Smith, 1994).

### **1.2.B. Climate and drainage system**

The development of a rift system had an important influence on the evolution of climate and drainage patterns in Kenya (Pickford, 1990).

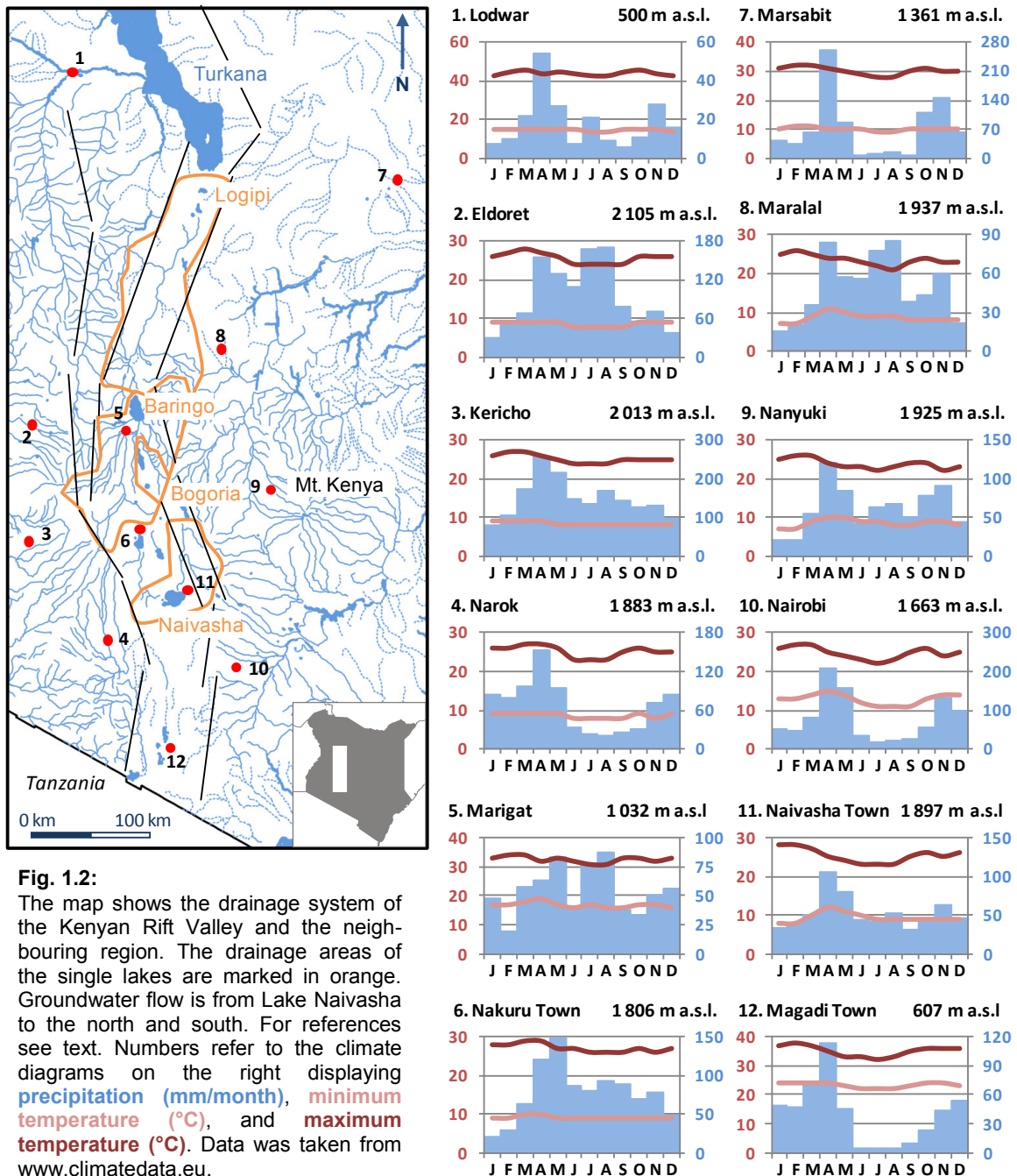
The migration of the ITCZ and air circulations from the Congo Basin have significant influences on the climate in the Kenyan Rift Valley, which lies in between those two climate systems (Nicholson, 1996). The migration of the ITCZ causes two rain seasons, one from March to May ('long rains') and a second one from October to December ('short rains'; *Kenya Meteorological Department*), with regional variations. The rift flanks act as natural barriers for the air masses, causing higher precipitation rates on the plateaus surrounding the rift than in the rift valley itself with up to 2 000 mm/a (Dunkley et al., 1993; Becht et al., 2006; Bergner et al., 2009; see also fig. 1.2). Regions to the west of the rift show a more stable rainfall distribution which, in general, is also higher (Dunkley et al., 1993). Precipitation rates in the rift are highest in Nakuru Town with 923 mm/a and decrease towards the north and south. The lowest values can be found in Lodwar in the north with 220 mm/a and in Magadi Town in the south with 469 mm/a. In the last couple of years, higher precipitation rates have caused rising lake levels, which flooded nearby villages (communicated orally by locals; see also fig. 1.4).

Temperatures in the rift are usually high, with the lowest values found in Naivasha Town (25 °C) and rising towards the north and south. The highest values are recorded in Lodwar with 44.1 °C in the north and in Magadi Town with 34.9 °C in the south. Due to higher temperatures, potential evaporation is also increasing from 1 900 mm/a in the centre of the rift (Bergner et al., 2003) to 4 000 mm/a at Lake Logipi (Dunkley et al., 1993; Junginger, 2011).

The flanks of the Kenyan Rift act as watersheds, thus creating a closed drainage system within the rift which is divided into seven sub-basins by faults and volcanic edifices (Dunkley et al., 1993; Mathu and Davies, 1996; Odada et al., 2005). Those faults and edifices determine the flow patterns of the rivers, which are mainly seasonal (Dunkley et al., 1993; Mathu and Davies, 1996). Examples for seasonal rivers are Suguta and Ol Arabel Rivers. Additionally, there are also some permanent ones, like the Kerio and Malewa Rivers which originate from the precipitation-rich rift flanks. Additionally, the faults divide the rift valley into a number of distinct groundwater aquifers corresponding to the location of the rift lakes. These are, from north to south, the aquifers Turkana, Baringo-Bogoria, Nakuru-Elementaita-Naivasha, and Magadi (Kuria, 2013). The drainage system can therefore be described as a chain of closed drainage basins (see fig 1.2). The aquifers are recharged by precipitation coming mainly from the rift flanks and infiltrating into the fractured volcanic rocks (Becht et al., 2006; Kuria, 2013). In general, groundwater flows from high-elevation lakes to lakes lying in lower altitudes. In case of the Kenyan Rift Valley, groundwater flows in deep aquifers from Lake Naivasha to Lakes Magadi and Bogoria in the south and north, respectively (Becht et al., 2006). Additionally, Lake Naivasha is connected to Lake Sonachi. This is assumed due to simultaneous lake-level oscillations in both lakes (Verschuren, 1999a). It is believed that there is a shallow aquifer linking Lake Naivasha to Lakes Elementaita and Nakuru, although the latter is more locally recharged (Becht et al., 2006). The aquifer Nakuru-Elementaita-Naivasha is only weakly connected to the Baringo-Bogoria aquifer (Kuria, 2013). The Kapedo Springs west of Mt. Silali represent the origin of the Suguta River which flows northward to Lake Logipi (Rhemtulla, 1970; Dunkley et al., 1993; Becht et al., 2006). The latter represents the terminal drainage point of the northern valley (Dunkley et al., 1993). Lake Logipi receives additional groundwater from Lake Turkana through the fractured rocks of the Barrier Volcanic Complex (also called the Barrier; Becht et al., 2006). Becht et al. (2006) state that Lake Logipi cannot be the terminal drainage point for the northern part of the Kenyan Rift, because large soda deposits like in the Lake Magadi area are missing. Further, Åse and Sernbo (1986) speculated that underground seepage from Lake Naivasha is prevented by an impermeable clay layer located in the sediment columns of Lake Naivasha and its satellite lakes.

Missing outlets, low precipitation, and high evaporation rates caused the Kenyan rift lakes to become very saline and alkaline. Additionally, the catchment areas of the lakes are quite small. The two freshwater Lakes Baringo and Naivasha maintain their freshwater character, because of larger catchment areas and, probably, underground water loss (Dunkley et al., 1993; Stoof-

Leichsenring et al., 2011). Lakes Logipi, Bogoria, Elementaita, and Magadi receive their major input from springs, whereas Lakes Turkana, Baringo, Nakuru, and Naivasha are mainly recharged by perennial rivers and ephemeral streams during the rainy season (Becht et al., 2006). Strong rainfall variability in the Kenyan Rift Valley causes the lake levels to fluctuate considerably over short- and also long-term time scales.



**Fig. 1.2:** The map shows the drainage system of the Kenyan Rift Valley and the neighbouring region. The drainage areas of the single lakes are marked in orange. Groundwater flow is from Lake Naivasha to the north and south. For references see text. Numbers refer to the climate diagrams on the right displaying precipitation (mm/month), minimum temperature (°C), and maximum temperature (°C). Data was taken from [www.climatedata.eu](http://www.climatedata.eu).

### 1.3. Motivation for this thesis

During the development of the East African Rift System, faults divided the rift into a number of smaller basins. Today, some of those basins contain rather small and shallow lakes. Although those lakes lie in close proximity to each other, their distinctness caused them to develop independently from each other. Differences in catchment size, precipitation, and evaporation are the reasons for huge hydrochemical differences between the lakes, varying from freshwater and low pH values to highly saline and alkaline conditions. Even on geologically short time scales, changing climatic conditions in East Africa caused the lake levels and hence salinity to change dramatically. Those changes are additionally accompanied by changes in the sedimentology of the deposited lake sediments and the composition of biota living in the lakes. Because of their unique character, the Kenyan rift lakes offer the exclusive opportunity to study a wide range of hydrogeochemical environments and the associated biogeochemical processes.

Most studies in the East African Rift System focus on the structural evolution of the rift and its influence on East African climate or they focus on lake-water properties, like temperature, pH, and biota. There are also studies which reconstructed the evolution of single lakes (e.g. Lake Suguta and the lakes in the Naivasha Basin) or lake-level changes (e.g. Lake Naivasha) with sedimentological means (see subchapter 1.4.D). But little is known about the hydro- and biogeochemical conditions in the underlying lake sediments.

Due to this missing knowledge, the primary aim for this thesis was to obtain data sets for different lakes in the Kenyan Rift Valley. Analyses of the sediment's porewater and biomarker composition were used to get a first general characterisation of the lake sediments. The gained data can be used to reconstruct the evolution of the single lakes and examine the influence of settlements, agriculture, and microorganisms on the lake chemistry. It was investigated how huge the influence of the lake chemistry is on the degradation of organic matter in the sediment column. Another important factor regarding the preservation of organic matter is the microbial activity, which we addressed by determining sulphate reduction rates, because sulphate is the most important electron acceptor in lake sediments. An additional aim of this study was to see if it is possible to distinguish between primary climate-induced signals and diagenetic overprints by microorganisms.

The following section gives an overview of the seven lakes in the Kenyan Rift Valley, which were studied during the course of this thesis. In chapter 2 the materials and methods are described in detail. Chapters 3 and 4 deal with the results of the inorganic and organic geochemical analyses performed on the lake sediments and their interpretation. The last chapter gives a summary of the work as well as an outlook.



## 1.4. Lakes of the study area

The study area is located in the Kenyan part of the East African Rift System (fig.1.6). In total seven lakes have been studied which differ in size, depth, catchment area as well as precipitation and evaporation rates. Because of this, the lakes vary in their hydrochemical properties, ranging from freshwater to very saline with varying pH values. Due to their location in the rift, the lakes can be put into three groups.

### 1.4.A. Lakes in the Suguta Valley



**Fig. 1.3:** Pictures of Lakes Logipi (left) and Eight (right) in the hot and dry Suguta Valley. In contrast to Lake Logipi, Lake Eight is a crater lake. Photos by A. Junginger

The Suguta Valley is located in the hot and dry northern part of the Kenyan Rift Valley. Temperatures can reach more than 50 °C (Dunkley et al., 1993) and precipitation is less than 300 mm/a (Castanier et al., 1993). The remote area is not inhabited by humans and is difficult to access due to a missing infrastructure (Tiercelin et al., 1987). The Suguta Valley hosts a small rift lake, called Lake Logipi, and some crater lakes situated in the dormant volcanoes in the valley. We studied one of those lakes, which is informally called Lake Eight, because of its shape (A. Junginger, personal communication).

#### *Lake Logipi*

Lake Logipi represents the remains of a much larger lake, which existed during Pleistocene times (Bosworth and Maurin, 1993; Castanier et al., 1993). The lake is now approximately 7.7 km long and 5.8 km wide (*Google Earth*), with a maximum depth of 3 to 5 m (Tiercelin et al., 1987). The water is highly saline (Tiercelin et al., 1987; Dunkley et al., 1993; app. 30 g/l in September 2012) and enriched in sodium bicarbonate (Mathea, 2009). Trona crusts, which are dissolved during wet periods (Tiercelin et al., 1987) can be found at the margins of the lake

(Mathea, 2009). It is mainly fed by hot springs which are located at the northern shore as well as in the vicinity of Naperito (also known as Cathedral Rock), an eroded tuff cone near the southern shore of the lake (Tiercelin et al., 1987; Dunkley et al., 1993). Those hot springs maintain a certain water level even during extreme arid times, when the lake shrinks considerably (Dunkley et al., 1993). Another water source during rain seasons is the Suguta River, which flows northward along the Suguta Valley (Dunkley et al., 1993), as well as the Losergoi and Akangbelai Rivers entering the lake from the east (Lambiase and Bosworth, 1995). A small amount of water might also originate from Lake Turkana in the north, which is separated from Lake Logipi by the Barrier Volcanic Complex, but this still has to be proven (Tiercelin et al., 1987; Dunkley et al., 1993). Lake Logipi is located in the lowest part of the rift valley with an altitude of 270 m.a.s.l (Dunkley et al., 1993) and is heavily populated by flamingoes (Mathea, 2009).

#### *Lake Eight*

In contrast to Lake Logipi, Lake Eight is a crater lake located in a maar in the Kangirinyang area around 60 km south-south-west of Lake Logipi in the southern part of the Suguta Valley. The lake is approximately 200 m long and 100 m wide (*Google Earth*) with a water temperature of about 27 °C. Due to a huge amount of algae, the colour of the saline water is bluish green. A lot of freshwater hot springs are located on the northern and western shores of the lake. Deep red crusts of trona can be found in highly alkaline pools on the southern margin of the lake (all info from Dunkley et al., 1993).

#### **1.4.B. Lakes in the Baringo-Bogoria Basin**

The Baringo-Bogoria Basin is located approximately 190 km south of Lake Logipi. In contrast to the latter, the area around those two lakes is populated by roughly 162 000 people (*Kenya Open Data*). The economy is mainly based on agriculture, producing maize, sweet potatoes, pigeon peas, and beans as food crops, as well as coffee, cotton, macadamia, and pyrethrum for export. Production of honey (Gichora et al., 2001) and fishing (Burnett and Rowntree, 1990) additionally represent important incomes for the people.

Two lakes are located in that basin, Lakes Baringo and Bogoria, and despite their proximity they are quite different regarding their hydrochemical properties. Climate in the area is hot and dry, although not as extreme as in the Suguta Valley. Marigat, a town located between the lakes, has an average annual maximum temperature of 32.4 °C and a mean precipitation of 652 mm/a ([www.climatedata.eu](http://www.climatedata.eu)).



**Fig. 1.4:** Pictures of Lakes Baringo (left) and Bogoria (right). Both lake levels were much higher due to high precipitation rates. Photos by S. Grewe

### *Lake Baringo*

Lake Baringo is located at an altitude of 970 m.a.s.l. and is one of two freshwater lakes in the Kenyan Rift (Tarits et al., 2006). It is approximately 21 km long, 10 km wide (*Google Earth*), on average 4 to 6 m deep (Dunkley et al., 1993), and is surrounded by littoral marshes and peripheral mudflats (Tarits et al., 2006). Several islands are located in the northern and central part of the lake (Tarits et al., 2006), the largest one being Ol Kokwe Island, an extinct volcano (Dunkley et al., 1993). Main inputs of water are through precipitation, hot springs, fumaroles (around Ol Kokwe Island) as well as drainage from permanent (e.g. Molo, Perkerra) and seasonal rivers (e.g. Endao, Makutan; Tiercelin et al., 1987; Odada et al., 2005). The drainage area is around 6 200 km<sup>2</sup> (Tiercelin et al., 1987) and is bounded by the Laikipia Plateau to the east, the Eldama Ravine to the south, and the Tugen Hills to the west (Odada et al., 2005). The lake does not have a surface outflow, but since Lake Baringo is located in an area with high evaporation rates, there has to be a significant subsurface outflow to sustain its freshwater character (Dunkley et al., 1993; Tarits et al., 2006). Studies suggest that part of the lake water is lost by groundwater seepage through the fractured lake floor towards the north (Tarits et al., 2006). The lake water has a sodium-carbonate composition and a surface temperature of 25 to 28 °C (Tiercelin et al., 1987). Lake Baringo is further characterised by high sedimentation rates, caused by high suspension loads of the rivers (Tarits et al., 2006).

### *Lake Bogoria*

Lake Bogoria, on the other hand, is an extremely saline and alkaline lake (Renaut and Tiercelin, 1993) at an altitude of 990 m.a.s.l. (Tiercelin et al., 1987). The lake is located in the Lake Bogoria Nature Reserve and is approximately 18 km long, 4 km wide (*Google Earth*), and 12.5 m deep (in 2012; De Cort et al., 2013). Because of its relative deepness, it is stratified and therefore hydrologically more stable than other rift lakes (Harper et al., 2003). Around 200 hot

springs, fumaroles, and geysers represent the main inflow for this lake (Tiercelin et al., 1987). The hot springs are located on the shores as well as on the lake floor (Mathea, 2009). Other inflows are through precipitation and some rivers (e.g. Wageses; Tiercelin et al., 1987), which run through agricultural productive land on the plateaus before entering the lake (UNESCO). The drainage basin of Lake Bogoria is much smaller than the one of Lake Baringo (705 km<sup>2</sup>; Tiercelin et al., 1987). Due to high evaporation rates and a missing outlet, the water of Lake Bogoria is extremely saline (Tiercelin et al., 1987). The lake has a very high productivity (Harper et al., 2003) with *Arthrospira fusiformis* being the dominant phytoplankton species in the lake and the main food for the Lesser Flamingoes occupying the shores.

#### **1.4.C. Lakes in the Naivasha Basin**

The Naivasha Basin is located on top of the Kenyan Dome approximately 80 km northwest of Nairobi. It is bordered, from north to west, by the Eburru Hills, the Kinangop Plateau, Mount Longonot, and the Mau Escarpment (Otiang'a-Owiti and Oswe, 2007). Three lakes are located in the basin: the main Lake Naivasha, its satellite Lake Oloiden, and the crater lake Lake Sonachi. Around 376 000 people live in the vicinity of the lakes (*Kenya Open Data*). The area is strongly influenced by agri- and floriculture; especially roses, carnations, and lilies are grown (*Kenya Flower Council*). The Olkaria Power Plant is located south of Lake Naivasha and produces geothermal energy.

##### *Lake Naivasha*

The lake has the highest altitude of all lakes in the Kenyan Rift Valley with an altitude of 1 885 m.a.s.l. (Olaka et al., 2010). Its volcanic-tectonic origin accounts for its relatively circular shape (Olaka et al., 2010). The lake is around 14.5 km in diameter (*Google Earth*) and has a maximum depth of around 8 m (Bergner et al., 2009). Crescent Crater, a partially submerged crater in the south-eastern part, represents the deepest part of the lake (approximately 18 m; Olaka et al., 2010). The freshwater lake (Bergner et al., 2009) is mainly fed by rivers (e.g. Malewa, Gilgil), which drain an area of around 3 400 km<sup>2</sup> (Stoof-Leichsenring et al., 2011). Estimations assume that approximately 15 % of the river input is lost due to underground seepage through the underlying volcanic rocks (Stoof-Leichsenring et al., 2011). Some of this water flows into Lake Oloiden located south-west of Lake Naivasha (Stoof-Leichsenring et al., 2011). The lake experiences large lake-level fluctuations due to precipitation changes in its catchment (Hubble and Harper, 2002). Unregulated irrigation, mainly through floriculture, usage of pesticides, and introduction of new species also has a large impact on the lake (Hubble and Harper, 2002; Becht et al., 2005). It is hypothesised that the geothermal power plant, located in the Olkaria Volcanic Complex, is also extracting water from the lake (Darling et al., 1996;



**Fig. 1.5:** The picture on the left shows Lake Oloiden. Lake Naivasha is located directly behind the sill in the background. The picture on the right side shows Lake Sonachi. Photos by S. Grewe

Ojiambo et al., 2001). Fauna in and around the lake includes hippopotamuses, giraffes, zebras, fish, and birds (Becht et al., 2005).

#### *Lake Oloiden*

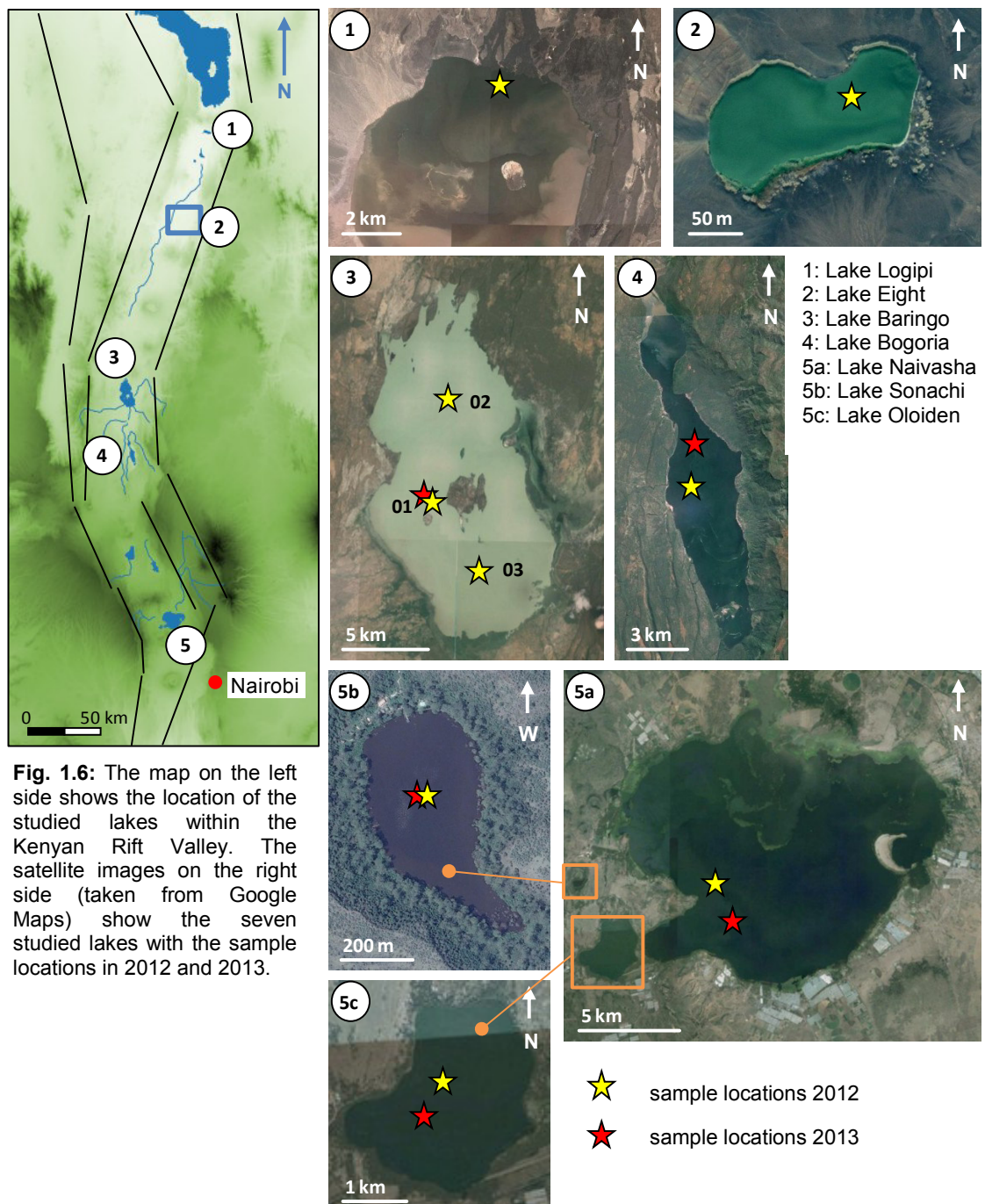
Lake Oloiden used to be a bay of Lake Naivasha during times of high water levels and lies directly southwest of the main lake (Uku and Mavuti, 1994). Due to generally decreasing water levels, the two lakes are now separated by a permeable sill (Verschuren et al., 1999b; Olaka et al., 2010). In the 1960s, a boat canal was built to reconnect Lake Oloiden with Lake Naivasha, but it was soon blocked by vegetation (Uku and Mavuti, 1994). The lack of water inflow from the main lake results in highly saline and alkaline conditions in Lake Oloiden (Uku and Mavuti, 1994). According to Harper and Mavuti (2006), conductivity in the lake increased from 250  $\mu\text{S}/\text{cm}$  in 1982 to 3 000  $\mu\text{S}/\text{cm}$  in 2005. The lake has an area of 5.5  $\text{km}^2$  (Uku and Mavuti, 1994) and a mean depth of 4 to 5.6 m (Uku and Mavuti, 1994; Otiang'a-Owiti and Oswe, 2007). The lake has no direct inflow and is hydrologically closed (Verschuren et al., 1999b; Verschuren, 2001), but satellite images show a narrow canal connecting Lakes Oloiden and Naivasha (Google Earth; coordinates: 0°48'54"S, 36°17'27"E).

#### *Lake Sonachi*

A second lake in the vicinity of Lake Naivasha is Lake Sonachi, also known as Crater Lake (Becht et al., 2005). It lies in a caldera of a small volcano whose steep walls are covered by dense forests (Becht et al., 2005). Because of its position in a caldera, Lake Sonachi has its own microclimate. The lake is highly alkaline with a high production of biomass (Becht et al., 2005). The lake covers an area of 0.6  $\text{km}^2$  and has an average depth of 3.8 m (Otiang'a-Owiti and Oswe, 2007). Although it is independent from the main lake, the lake level of Lake Sonachi seems to follow the one of Lake Naivasha, because of a groundwater connection (Verschuren,



2001; Harper and Mavuti, 2006). If the lake level reaches 5 m or more, the lake gets chemically stratified (Verschuren, 1999a).



#### 1.4.D. Former studies on the lakes

The lakes in the Kenyan Rift Valley were intensively studied. Most of the studies deal with physical and chemical parameters of the lake water, their variability through time, or with socioeconomic problems. This paragraph gives a small overview of completed studies.

Sediment cores of Lake Naivasha, for example, have been used to reconstruct lake-level and climate changes (Verschuren et al., 2000; Verschuren, 2001). Stoof-Leichsenring et al. (2011) used a 200-year old core to determine the human influence on Lake Naivasha using total phosphorous, nitrogen, and carbon contents as well as diatoms as proxies. The footprint of the flower industry on Lake Naivasha was studied by Otiang'a-Owiti and Oswe (2007) and Mekonnen et al. (2012). Hubble and Harper (2002) looked at changes in phytoplankton in the lake within a time period of one year. Other studies deal with the water budget and the amount of groundwater outflow from Lake Naivasha (e.g. Åse, 1987; Darling et al., 1990). Neighbouring Lakes Oloiden and Sonachi have been studied for changes in algae and invertebrate communities (Verschuren et al., 1999a; Verschuren et al., 1999b). The influence of lake depth and mixing regime on patterns of sedimentation were studied in Lake Sonachi (Verschuren, 1999a). Verschuren (1999b) compared the lithological stratigraphy from all four lakes in the Naivasha Basin and determined the influence of basin morphology and physical limnology on the preservation and time resolution of sedimentary climate-proxy records.

Studies on Lakes Baringo and Bogoria also focus on physical and chemical parameters (e.g. Oduor et al., 2003; Tarits et al., 2006) as well as sinter and chert deposits around sublacustrine hydrothermal vents (Renaut and Owen, 1988; Renaut et al., 1998; Renaut et al., 2002).

Studies on Lake Logipi are rare. Castanier et al. (1993) studied the effects of microbial activity on the lake water chemistry. Other studies on Lake Logipi deal with its precursor Pleistocene lake (Junginger, 2011) or the supposed underground seepage from Lake Turkana (Nunn and Harris, 2007).

Other studies focus on the tectonic influence on the evolution of rift lakes and their drainage systems (Bergner et al., 2009) or the groundwater links between the single lakes (Becht et al., 2005). Olaka et al. (2010) compared the basin morphology of East African lakes with their ability to record climate changes.

During the course of this thesis, additional datasets were gained, which can now be integrated into the already existing network. Since little is known about the hydro- and biogeochemical conditions in the lake sediments, these datasets, consisting mainly of porewater and biomarker data, will improve our knowledge about the influence of human activity on the lakes as well as influences of microorganisms on the lake chemistry and vice versa.





The background features three large, solid yellow circles of varying sizes. One is in the top right, one is in the middle right, and one is in the bottom right. Two thin yellow lines cross the page diagonally, one from the top left to the middle right, and another from the top right to the bottom right.

## **Chapter 2:**

## **Materials and methods**



## 2.1. Coring and sampling

On the first field campaign in September 2012, multiple cores from seven lakes in the Kenyan Rift Valley were taken, namely Lakes Naivasha, Oloiden, and Sonachi in the Naivasha Basin, Lakes Baringo and Bogoria in the central part of the rift, as well as Lakes Logipi and Eight in the northern part of the Suguta Valley. The cores were taken with a Kajak Corer (KC Denmark Research Equipment, Silkeborg, Denmark) from the deepest part of each lake in order to get long and undisturbed sediment records. At Lake Baringo, cores were taken at three different locations with increasing distance from the southern shore, where a number of rivers flow into the lake (e.g. Perkerra, Ol Arabel, El Molo). The exact coring sites are shown on the satellite images in figure 1.6. The sediment cores varied in length from 45 to 80 cm and were subsampled onsite into 2 cm (upper 10 cm) and 5 cm intervals (rest of the core), respectively. For porewater analysis, the water of each subsample was squeezed out with a hydraulic porewater press (KC Denmark), captured in a syringe, filtered with a 0.2  $\mu\text{m}$  filter, and divided into four aliquots, each stored in small cryovials and containing 0.5 – 2 ml of water. Depending on further analysis (e.g. ion analysis), different chemical preservatives were added to each aliquot group (see subchapter 2.2). The remaining sediment, also called squeeze cake, was stored in plastic bags and used to determine different reduced inorganic sulphur species in the sediment (see subchapter 2.3.A). Additionally to the cores, water samples from the surface and the bottom of the lakes were taken to compare their salinity and ion composition with the one of the sediment's porewater. Conductivity (Conductivity Meter 7032/2; Tunze GmbH, Germany), salinity (PCE-028 Refractometer; PCE Instruments, Germany), and pH (Knick Portames 654; Knick, Germany) of the lake water were also determined in the field. Back in Germany, pH field values were confirmed by using pH indicators on lake water samples.

During the second field campaign in September 2013, cores from Lakes Naivasha, Oloiden, Sonachi, Baringo, and Bogoria were taken for organic geochemical analysis (see subchapter 2.4) and the determination of sulphate reduction rates (SRR; see subchapter 2.3.B). Due to stronger winds on the lakes and hence stronger currents, it was not always possible to core at the same sites as in 2012 (fig. 1.6). The cores were similar in length as in the year before and were subsampled in the same intervals. After porewater samples were taken with the same method as in 2012, the squeeze cakes were stored in aluminium bags for geochemical analysis. For the determination of SRR, sub-cores from the undisturbed inner part of the core were retrieved with small glass cylinders (app. 5 cm<sup>3</sup>). Three samples of each depth interval were taken. The glass cylinders were sealed with rubber plugs and stored in aluminium bags flushed with nitrogen (N<sub>2</sub>) to avoid oxidation of the sediment.

In Germany, the samples for porewater analysis and SRR were stored in the fridge, whereas the squeeze cakes were stored in the freezer. Fig. 2.1 gives an overview of the subsequent lab procedure.

### *Calibration of the salinity refractometer*

The salinity refractometer was calibrated in the field against sodium chloride (NaCl) solutions with different salinities. Because hydrogen carbonate ( $\text{HCO}_3^-$ ) is the most abundant ion in the lakes, instead of  $\text{Na}^+$  like in most other waters, the gained values are not accurate, but they gave a first impression in the field.

## **2.2. Lake and porewater analysis**

### **2.2.A. Ion composition of the porewater**

Two aliquots of the porewater samples were used for the identification of different ions within the sediment's porewater. The aliquot for anion analysis was left untreated, whereas 20  $\mu\text{l}$  of hydrochloric acid (HCl; 18.5 %) were added to each aliquot for cation analysis to prevent carbonate precipitation. Significant amounts of carbonate were found in the majority of samples, causing them to foam when HCl was added. Depending on their salinity, the samples were diluted (for dilution factors see table 2.1) with deionised water and measured on an ion chromatograph (IC). The analytical parameters are listed in table 2.2.

Keratin, an important constituent of feathers, most likely hindered the cation analysis of water samples from Lake Logipi. A large number of flamingoes populate the shores of the lake, losing feathers, which are readily dissolved in the highly alkaline water. The keratin in the water reacts with the coating of the IC column and stays there, blocking the separation of the cations. In order to solve the problem, the water samples of all lakes have been diluted in a weak sulphuric acid (5 mM  $\text{H}_2\text{SO}_4$ ) instead of deionised water. In total, 145 porewater samples have been analysed for their ion composition. Each sample was measured in duplicate (50  $\mu\text{l}$  each) and analysed for the following ions: fluoride ( $\text{F}^-$ ), chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), sulphate ( $\text{SO}_4^{2-}$ ), potassium ( $\text{K}^+$ ), sodium ( $\text{Na}^+$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), and ammonium ( $\text{NH}_4^+$ ). An unidentifiable cation eluted directly before  $\text{Ca}^{2+}$  in all saline lakes. Because the cation measurements of the two freshwater Lakes Baringo and Naivasha did not, for unknown reasons, deliver usable results, the data has been excluded. In both cases, different dilution factors and eluents could not solve the problem. The standard deviation for 85.01 % of the measurements was less than 5 %. For 9.41 % the standard deviation was 5 – 10 %; for the remaining 5.58 % it was more than 10 %.

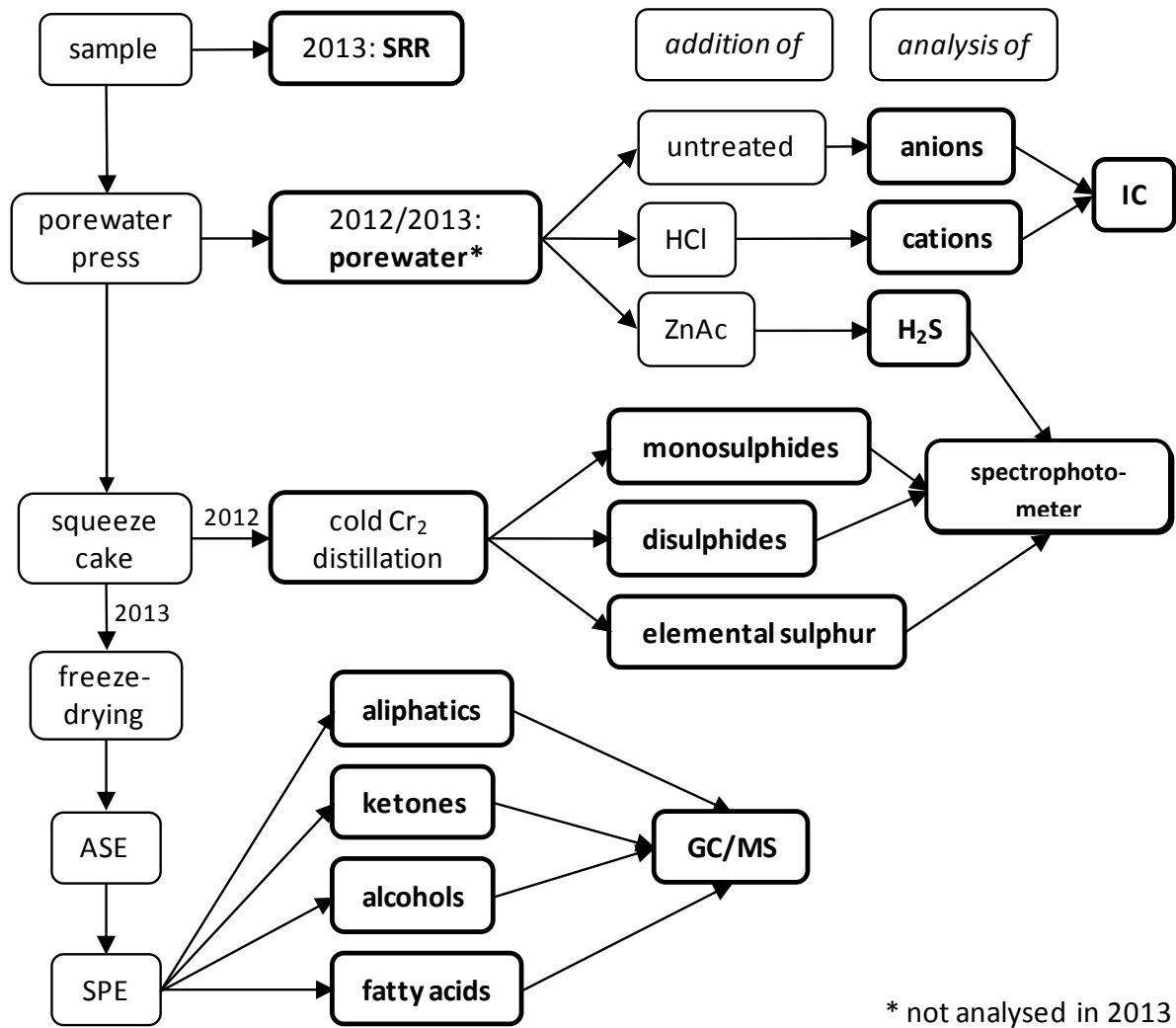


Fig. 2.2: Flow chart summarising the methodological pathway.

Table 2.1: Table showing the dilution factors used for porewater analysis.

Lake	dilution anions <sup>1</sup>	dilution cations <sup>3</sup>
Logipi	1 : 200	1 : 500 (0 – 15 cm); 1 : 1 500 (15 – 40 cm); 1 : 2 000 (40 – 55 cm)
Eight	1 : 50	1 : 1 000
Baringo	1 : 1	1 : 1 & 1 : 10 <sup>4</sup>
Bogoria	1 : 50 / 1 : 2 <sup>2</sup>	1 : 1 000
Naivasha	1 : 1	1 : 50 <sup>4</sup>
Oloiden	1 : 2	1 : 50
Sonachi	1 : 5	1 : 200

<sup>1</sup> in deionised water <sup>2</sup> for phosphate; <sup>3</sup> in 5 mM H<sub>2</sub>SO<sub>4</sub>; <sup>4</sup> measurements did not deliver usable results

**Table 2.2:** Table showing the analytical parameters for ion chromatography.

	<b>anions</b>	<b>cations</b>
<b>instrument</b>	Sykam IC (Sykam Chromatographie Vertriebs GmbH, Germany)	
<b>suppressor</b>	SAMS™, SeQuant, Sweden	none
<b>detector</b>	Sykam S3115 conductivity detector	Sykam S3115 conductivity detector & Sykam S2500 UV detector
<b>column</b>	LCA A14	Dionex IonPac CS14
<b>eluent</b>	2.5 mM Na <sub>2</sub> CO <sub>3</sub> + 1 ml/l modifier (1 g 4-hydroxybenzonitrile in 50 ml methanol)	5 mM H <sub>2</sub> SO <sub>4</sub>
<b>flow rate [ml/min]</b>	1.0	1.0
<b>oven temperature [°C]</b>	65	40
<b>elution type</b>	isocratic	isocratic
<b>analysis time [min]</b>	12	12

### 2.2.B. Hydrogen sulphide in the porewater

In order to fix the volatile hydrogen sulphide (H<sub>2</sub>S) as zinc sulphide (ZnS), 100 µl of zinc acetate solution (ZnAc; 200 g/l) were added to each aliquot. The concentration of H<sub>2</sub>S in the water was determined using the method of Cline (1969). Therefore, 10 or 20 µl of the homogenised sample was transferred into a glass vial containing 5 ml of deionised water. 400 µl of a freshly mixed reagent containing 1.6 g of *N,N*-dimethyl-*p*-phenylenediamine sulphate and 2.4 g of iron(3+) chloride hydrate (1:3:6) in 100 ml of 18.75 % HCl was added and the vial capped. After 20 min the absorbance was determined spectrophotometrically (Ultrospec 4000, Pharmacia Biotech, England) at 670 µm. Two aliquots from each of the 108 samples were measured in triplicate. To test whether the remaining ZnAc solution in the vials would hinder the measurements, pure ZnAc solutions with roughly the same salinity as our water samples (5.28 %, 3.36 %, and 1.43 %) were analysed prior to sample analysis. The results showed that, at the concentration levels found in the samples, ZnAc did not interfere with the spectrophotometric quantification of H<sub>2</sub>S. The H<sub>2</sub>S concentrations in Lakes Baringo, Naivasha, and Oloiden were below the detection limit, even though higher sample amounts were used. For the remaining lakes, the standard deviation for 73.68 % of the measurements was less than 5 %. For 23.62 % the standard deviation was 5 – 10 %.

## 2.3. Dissimilatory sulphate reduction

### 2.3.A. Total reduced inorganic sulphur (TRIS)

In order to separate the reduced sulphur compounds from the sediment, a multi-step version of the distillation method of Kallmeyer et al. (2004) was applied. With that method, TRIS species are liberated by mixing the sediment sample with HCl, chromous chloride ( $\text{CrCl}_2$ ), and dimethylformamide (DMF), while purging nitrogen gas ( $\text{N}_2$ ) into the mix. The single chemicals liberate individual sulphur species, which are then transported as  $\text{H}_2\text{S}$  by the  $\text{N}_2$  into a ZnAc trap, where the  $\text{H}_2\text{S}$  precipitates as ZnS.

For this study, between 1 and 5 g of sample material was used, depending on the amount available. Instead of adding all chemicals at once, like in the original method, they were added successively to liberate the individual sulphur species separately. Acid-volatile sulphur (AVS, i.e. free  $\text{H}_2\text{S}$  and FeS) was liberated using 8 ml of 6 M HCl. The sediment-HCl mix was stirred for two hours, before 16 ml of 1 M  $\text{CrCl}_2$  were added to remove the chromium-reducible sulphur (CRS, i.e.  $\text{FeS}_2$ ,  $\text{S}^0$ ). Chemically resistant elemental sulphur (ES) was liberated by adding 20 ml of DMF. After every addition of chemicals, the sediment mix was stirred for two hours and the ZnAc (7 ml, 5 % (w/v)) trap was exchanged. The content of each trap was transferred into 15 ml falcon tubes and then centrifuged for 15 min with 4 000 rpm. The supernatant was carefully decanted off and discarded. The remaining ZnS pellet was resuspended in 7 ml of deionised water. In order to determine the amount of sulphide in each sample, its concentration was analysed according to the method of Cline (1969; see also subchapter 2.2.B). For most of the 156 samples from Lakes Sonachi, Bogoria, Logipi, and Eight, 10 or 20  $\mu\text{l}$  of ZnS suspension were sufficient for analysis. Some samples required larger amounts of up to 50  $\mu\text{l}$ . Since  $\text{H}_2\text{S}$  concentrations in the porewater were below the detection limit in Lakes Naivasha, Oloiden, and Baringo, sulphide compounds were not determined. The standard deviation for 78.21 % of the measurements was less than 5 %. For 21.79 % the standard deviation was 5 – 10 %.

### 2.3.B. Sulphate reduction rates (SRR)

For the determination of SRR, three samples (each 2.7 – 7.3 g) per depth interval were taken and incubated using the whole-core-incubation method of Jørgensen (1978). In Potsdam, the samples were stored in the fridge for approximately 3 months. After acclimating the samples in a water bath ( $30\text{ }^\circ\text{C} \pm$  lake-water temperature) for three days to reactivate the microbial metabolism, 15  $\mu\text{l}$  of  $^{35}\text{S}$ -labelled sulphate tracer (activity: 1 MBq) were injected with a microlitre syringe. After 24 h of incubation time in the water bath, the samples were transferred into 10 ml of 20 % (w/v) ZnAc solution to terminate microbial activity and to precipitate all free  $\text{H}_2\text{S}$  as ZnS. The slurry was centrifuged to separate the sediment from the ZnAc solution and the porewater

( $\triangleq$  supernatant). The supernatant contained all unconsumed sulphate tracer, whereas the sediment pellet contained the microbially reduced tracer in form of AVS, CRS, and ES ( $\triangleq$  TRIS). TRIS was liberated using the single-step cold chromium distillation of Kallmeyer et al. (2004; see also subchapter 2.3.A). Radioactivity of TRIS and the supernatant was measured using liquid scintillation counting (Tri-Carb 2800TR, PerkinElmer, USA) with a counting window of 4 – 160 keV and Ultima Gold XR as scintillation cocktail. SRR were calculated using the following formula:

$$\text{SRR} = [\text{SO}_4^{2-}] \times P_{\text{SED}} \times \frac{a_{\text{TRIS}}}{a_{\text{TOTAL}}} \times \frac{1}{t} \times 1.06 \times 1000$$

In this formula,  $[\text{SO}_4^{2-}]$  is the  $\text{SO}_4^{2-}$  concentration in the sediment's porewater in [mmol/l],  $P_{\text{SED}}$  is the sediment's porosity (has been estimated to be 90 % in the normal sediment and 60 % in the desiccation horizons (Verschuren, 1999; De Cort et al., 2013)),  $a_{\text{TOTAL}}$  and  $a_{\text{TRIS}}$  are the total radioactivity and the radioactivity of TRIS in [counts per minutes  $\triangleq$  cpm] and  $t$  is the incubation time in [d]. The numbers 1.06 and 1000 are the fractionation factor for the expected isotopic fractionation (Jørgensen and Fenchel, 1974) and the factor converting [mmol/l] to [nmol/cm<sup>3</sup>], respectively. SRR are in [nmol/(cm<sup>3</sup> × d)]. The ratio of  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  is used to calculate how much of the labelled  $\text{SO}_4^{2-}$  tracer was turned over during incubation. Since the tracer mixes completely with the non-radioactive  $\text{SO}_4^{2-}$  already present in the sediment, this ratio also provides the mean to determine the amount of  $\text{SO}_4^{2-}$  consumed during the incubation. According to Fossing (1995), the ratio of  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  should not exceed 0.01, because if it does the necessary linear relationship between incubation time and decrease of radioactivity cannot be guaranteed, which leads ultimately to unreliable SRR. However, it has been shown that ratios not exceeding 0.1 are also still acceptable.

## 2.4. Organic geochemistry

For the analyses in organic geochemistry, all used equipment, like glassware and silica gel, was combusted before usage to clean them from any organic particles. For the same reason, the cellulose filters were extracted in advance with dichloromethane (DCM).

### 2.4.A. Accelerated solvent extraction (ASE)

The 77 frozen sediment samples were freeze-dried for three days (Christ Alpha 1-2 LD plus, Martin Christ Gefriertrocknungsanlagen GmbH, Germany) and then the biomarkers were extracted using accelerated solvent extraction (ASE; Dionex ASE 350, Dionex Inc., USA). About 1.5 to 15 g of the fine-grained sample were mixed with diatomaceous earth to avoid blocking



and hence leakage of the cell. The selected operating conditions for the extraction were as follows: temperature 100 °C, pressure 75 bar, preheating period 5 min, static extraction period 12 min, solvent flush 100 % of cell volume, N<sub>2</sub> purge 90 s, and number of cycles 2. The solvent was a DCM/MeOH (methanol) mix of 9:1. The final extraction volume was approximately 60 ml. The extracts were then flushed with N<sub>2</sub> in order to accelerate evaporation of the solvent. The residue was then resuspended in roughly 4 ml of DCM in a small glass vial.

#### 2.4.B. Solid phase extraction (SPE)

The different biomarker fractions contained in the extracts were separated using solid-phase extraction (SPE). Therefore, SPE tubes were filled with 3 g of silica gel, which was activated before usage in an oven at 50 °C for at least 24 h. Meanwhile, the extracts were again flushed with N<sub>2</sub> to evaporate the solvent and then resuspended with a few drops (~ 300 µl) of *n*-hexane. Before the samples were added to the columns, the latter were conditioned with approximately 4 ml of *n*-hexane. Successively, solvents with increasing polarity were added to obtain different compound fractions: 12 ml of *n*-hexane (F1  $\triangleq$  e.g. *n*-alkanes, steranes), 15 ml of *n*-hexane/DCM 4:1 (F2  $\triangleq$  e.g. ketones), and 25 – 30 ml of DCM/MeOH 9:1 (F3  $\triangleq$  e.g. alcohols, fatty acids). The three different fractions were captured in separate glass vials. After flushing them again with N<sub>2</sub>, the fractions were transferred into GC vials and dissolved in *n*-hexane (F 1) and DCM (F 2 and F 3), respectively.

In a second step, the third fraction (F3) was separated into alcohols and fatty acids with a second column chromatography. The procedure was the same as described above, but aminopropyl silica instead of normal silica gel was used in order to improve the separation. The alcohols ( $\triangleq$  F3) were eluted with 15 ml of a DCM/acetone mix (9:1) and the fatty acids ( $\triangleq$  F4) with 25 ml of DCM containing 2 % of formic acid. Both fractions were treated with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) in DCM at 75 °C for 60 min to form trimethylsilyl esters of the compounds, which are more stable during GC analysis.

#### 2.4.C. Gas chromatography/mass spectrometry (GC/MS)

The four fractions were measured on a GC/MS (Agilent 7890A GC System with GC-FID & 5975C MSD, Agilent Technologies Inc., USA). 1 µl of the sample was injected into a programmable temperature injector (PTV). After 2.5 min the injector was heated to 300 °C with a rate of 720 °C/min. Separation was achieved on an HP-5MS column (29.8 m x 250 µm, film thickness 0.25 µm) using helium as a carrier gas. The oven temperature remained at 70 °C for the first 2 min after the injection and was raised to 320 °C with a rate of 12 °C/min for F1 and F2 and with a rate of 5 °C for F3 and F4. The final temperature was held for 15 min. Total runtime

was 37 min for F1 and F2 and 67 min for F3 and F4, respectively. The MSD (mass selective detector) was operated in EI mode at 70 eV and scanning from 50 – 650 mass units. For the identification of compounds, obtained mass spectra were compared with spectra from NIST MS Search 2.0. Compounds were quantified using the FID (flame ionisation detector) trace of the chromatogram and the absolute amounts were calculated relative to the peak area of internal standards. As internal standards 5 – 20 µl of 5α-androstane (for F1 and F2) or (3β,5α)-androstane-3-ol (for F3 and F4) were added prior to GC/MS analysis.

The component amounts are given in µg/g of dry sediment weight (µg/g<sub>dry wt.</sub>).

### Quantification of compounds

There were some components where an identification was not possible, mainly due to low concentrations of the respective compounds. They are, however, included in the total biomarker concentration, which encompasses all quantified and unquantified compounds.

In order to name the identified components, the IUPAC (International Union of Pure and Applied Chemistry) nomenclature was used. In some cases, however, trivial names were used. If this was the case, it is marked in the respective tables, where the biomarkers are listed.

## 2.5. Overview of available data

**Table 2.3:** This table gives an overview of the data available for the single lakes.

Lake	porewater			sediment		
	anions	cations	H <sub>2</sub> S	TRIS	SRR	biomarkers
Logipi	✓	✓	✓	✓	✗	✗
Eight	✓	✓	✓	✓	✗	✗
Baringo	✓	✗	✗	✗	✓	✓
Bogoria	✓	✓	✓	✓	✓	✓
Naivasha	✓	✗	✗	✗	✓	✓
Oloiden	✓	✓	✗	✗	✓	✓
Sonachi	✓	✓	✓	✓	✓	✓

The page features a minimalist design with three large, solid red circles of varying sizes. One large circle is in the top right, a smaller one is in the middle right, and another large one is in the bottom right. Two thin red lines cross the page diagonally, one from the top left to the middle right, and another from the top right to the bottom right.

## **Chapter 3:**

# **Results and general characterisation of the lake sediments**



### 3.1. Introduction

#### 3.1.A. Ion composition of Kenyan lakes

In general, a combination of rock composition, volcanic activity, climate conditions, and anthropogenic activities in the drainage area determine the ion composition in the Kenyan rift lakes (Davies, 1996). Because of the endorheic nature of those lakes together with generally high evaporation rates in the rift (see subchapter 1.2.B), ions are enriched in the lakes' water.

The most dominant ions reported in Kenyan waters are sodium ( $\text{Na}^+$ ), hydrogen carbonate ( $\text{HCO}_3^-$ ), and fluoride ( $\text{F}^-$ ; e.g. Gaciri and Davies, 1993; Davies, 1996). The latter has its origin in the  $\text{F}^-$ -bearing rocks of the rift valley like, for example, mugearite (Nanyaro et al., 1984; Dunkley et al., 1993). Fluoride concentrations determined in this study of 1 mg/l in the freshwater lakes and of at least 190 mg/l in the saline lakes are above the global average of 0.01 mg/l to 0.3 mg/l for surface water (EHC 227, 2002) and, especially in the saline lakes, well above the recommended levels of the World Health Organization of 1.5 mg/l (WHO). Excessive uptake of  $\text{F}^-$  has severe consequences on health, mainly dental and skeletal fluorosis (WHO). The concentrations of calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) on the other hand are very low in all rift lakes (e.g. Gaudet and Melack, 1981; Dunkley et al., 1993; Gaciri and Davies, 1993), because they usually precipitate as carbonates within the catchment of the lakes (e.g. Castanier et al., 1993; Gizaw, 1996).

#### 3.1.B. The sulphur cycle

Sulphur is a component of numerous minerals, for example pyrite and pyrrhotite, and an essential element for organisms. The latter convert a huge amount of sulphur and sulphur compounds for energy gain and anabolism. Consequently, the sulphur cycle is of huge biogeochemical importance (fig. 3.1).

Dissimilatory sulphate reduction is an important process in the anaerobic degradation of organic material in marine and lacustrine sediments, where sulphate-reducing bacteria obtain energy by oxidising organic matter to  $\text{CO}_2$ , while simultaneously reducing sulphate ( $\text{SO}_4^{2-}$ ) to sulphide (Jørgensen, 1982; Berner et al., 1985). The latter either remains in solution as hydrogen sulphide ( $\text{H}_2\text{S}$ ), is oxidised to elemental sulphur (ES) by sulphide-oxidising bacteria, or it precipitates as mono- or disulphides (mainly  $\text{FeS}$  and  $\text{FeS}_2$ ; Berner et al., 1985; Rudd et al., 1986). Although most of those iron sulphides form where sulphate reduction occurs (Holmer and Storkholm, 2001), they can also precipitate elsewhere if dissolved  $\text{H}_2\text{S}$  diffuses out of the zone of sulphate reduction. Iron sulphides are either permanently buried or they are reoxidised by iron- and sulphide-oxidising bacteria and archaea (Schippers and Jørgensen, 2002 & references therein). It is also possible to oxidise sulphides chemically in the presence of iron

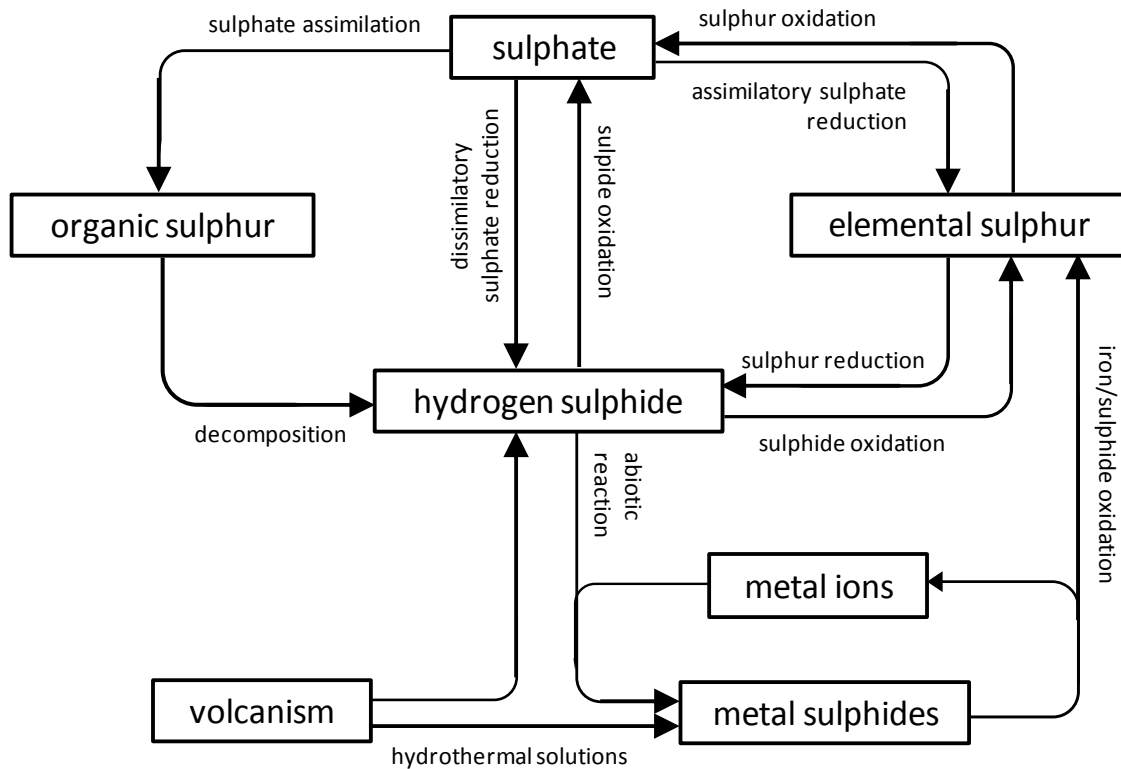


Fig. 3.1: The sulphur cycle. Modified after Brudersohn, Wikipedia

and manganese oxides and hydroxides, which are mixed into the anoxic sediment layer by bioturbation (Burdige and Nealson, 1986; Holmer and Storkholm, 2001 and references therein; Schippers and Jørgensen, 2001; Schippers and Jørgensen, 2002).

Sulphate reduction in marine systems is mainly controlled by the availability and reactivity of organic matter (Berner et al., 1985), whereas in freshwater lakes, the availability of  $\text{SO}_4^{2-}$  is more important, because  $\text{SO}_4^{2-}$  concentrations are generally low (Berner et al., 1985; Holmer and Storkholm, 2001).

### 3.1.C. Origin and assignment of biomarkers

Biomarkers are defined as 'lipid-derived compounds that can be traced to particular biological precursor molecules' (Killops and Killops, 2013). The most abundant ones among those biological molecules are *n*-alkanes, *n*-alkanols, *n*-fatty acids, hopanoids, and sterols (e.g. Kvenvolden, 1967; Cranwell, 1973; Bost et al., 2001; Killops and Killops, 2013). All those compounds are insoluble in water, but soluble in organic solvents (e.g. hexane or acetone), therefore also called lipids (Killops and Killops, 2013).

In young sediments, the distribution of biomarkers is strongly influenced by the relative contribution of autochthonous (from algae and bacteria) and allochthonous (from terrestrial sources) organic matter and the conditions in the sedimentary environment (e.g. oxygen

availability, salinity, trophic state). Therefore biomarker distributions can be used to differentiate between major organism groups contributing to young sediments and to reconstruct the depositional environment (Killops and Killops, 2013).

#### *Straight-chain compounds*

Straight-chain compounds, like *n*-alkanes, *n*-alkanols, and *n*-fatty acids, are among the most widely used biomarkers. They are found in waxes, oils, and fats where they act as protective coatings and energy stores (Kvenvolden, 1967; Kolattukudy, 1970; Killops and Killops, 2013).

The leaf waxes of higher plants usually consist of *n*-alkanes, *n*-alkanols, and *n*-fatty acids which range in length from 20 to 38 carbon atoms (*n*-C<sub>20</sub> to *n*-C<sub>38</sub>; Eglinton and Hamilton, 1967; Kolattukudy, 1970; Ishiwatari and Hanya, 1975; Matsuda, 1978; Grimalt et al., 1991). In this study, *n*-C<sub>25</sub> – *n*-C<sub>35</sub> alkanes, *n*-C<sub>24</sub> – *n*-C<sub>32</sub> alkanols, and saturated *n*-C<sub>20</sub> – *n*-C<sub>32</sub> fatty acids were attributed to higher plants.

In contrast to higher plants, algae and bacteria are usually characterised by straight-chain compounds shorter than *n*-C<sub>20</sub>. The dominant *n*-alkane is usually the *n*-C<sub>17</sub> (Han et al., 1968; Kolattukudy, 1970; Matsumoto et al., 1990), whereas *n*-alkanols and *n*-fatty acids are dominated by *n*-C<sub>16</sub> and *n*-C<sub>18</sub> (Cranwell, 1974; Ishiwatari and Hanya, 1975; Volkman et al., 1980; Kawamura and Ishiwatari, 1985; Grimalt et al., 1991). In this study, the *n*-C<sub>17</sub> alkane and the *n*-C<sub>16</sub> alkanol were attributed to an autochthonous input by algae and bacteria.

The two short-chain *n*-fatty acids *n*-C<sub>16</sub> and *n*-C<sub>18</sub> are found in almost all organisms and because of their ubiquity are hard to attribute to a certain group of organisms (e.g. Kvenvolden, 1967; Cranwell, 1974; Killops and Killops, 2013). Only in Lake Naivasha, those *n*-fatty acids could be safely attributed to bacteria. Furthermore, it was not possible to attribute the short-chain *n*-alkanols *n*-C<sub>15</sub>, *n*-C<sub>17</sub>, and *n*-C<sub>19</sub> to any organism.

#### *Hopanoids and Steroids*

Hopanoids and steroids represent two of the most abundant biomarkers in sediments (Innes et al., 1998; Härtner et al., 2005), because those molecules are relatively stable regarding degradation (Wen-Yen and Meinschein, 1976; Hassett and Lee, 1977; Prince et al., 1994; Martins et al., 2007). They act as membrane stabilisers in bacterial (hopanoids) and eukaryotic (steroids) organisms (Hassett and Lee, 1977; Härtner et al., 2005).

For a long time, it was assumed that hopanoids are only produced by aerobic bacteria (studies cited in Innes et al., 1998), but later studies showed that some facultatively anaerobic and strictly anaerobic bacteria can also produce hopanoids; although they remain in the minority (Härtner et al., 2005 and studies cited therein). Hopanoids are rarely found in other organisms than bacteria (Elvert et al., 2001; Killops and Killops, 2013) and therefore all hopanes found in the study were attributed to bacteria.

Sterols are commonly divided into phytosterols, produced by higher plants and algae, and zoosterols, produced by zooplankton and higher animals. In this study, it was difficult to assign the single sterols, since the sterol distributions may overlap in the single organism groups mentioned above. It was shown, that especially algae can contain significant amounts of zoosterols (Wen-Yen and Meinschein, 1976; Nishimura and Koyama, 1976; Volkman, 1986; Volkman, 2003). Additionally, not all core samples contained enough sterols to correlate them with other biomarkers. If present in sufficient amounts most phytosterols were mainly attributed to algae, as were cholesterol and its hydrogenated form, (3 $\beta$ ,5 $\alpha$ )-cholestan-3-ol.

### *Carotenoids*

Carotenoids are widely distributed, but are found in larger concentrations in photosynthetic organisms (Killops and Killops, 2013). Their most important functions are absorption of light energy for photosynthesis and protection from photodamage (Armstrong and Hearst, 1996). Carotenoids are subdivided into xanthophylls and carotenes, depending whether they contain oxygen or not (Killops and Killops, 2013).

The carotenoid structure detected in this study is probably derived from  $\beta$ -carotene which is in most cases not a specific marker for a certain group of organisms. In this study, however, the carotenoid structure was attributed to cyanobacteria, because 1) its precursor,  $\beta$ -carotene, is commonly found in cyanobacteria (Killops and Killops, 2013) and 2) because the carotenoid structure was only found in the saline lakes where those organisms are abundant (Verschuren, 1994; Verschuren et al., 1999a; Krienitz et al., 2003; Mavuti and Harper, 2006; Oduor and Schagerl, 2007; De Cort et al., 2013; Schneider, 2013).



## 3.2. Lake Logipi

### 3.2.A. Results

#### *Lake and porewater chemistry*

In Lake Logipi, conductivity of the bottom and surface water was equally high with 46 000  $\mu\text{S}/\text{cm}$  and 42 300  $\mu\text{S}/\text{cm}$ , respectively. Salinity and pH of the lake water were also similar with roughly 30 g/l and 9.8.

Dissolved ions found in the sediment porewater of Lake Logipi included  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  (see depth profiles in fig. 3.2).  $\text{H}_2\text{S}$  was also found. Almost all ion concentrations increased strongly with depth, although  $\text{K}^+$  concentrations fluctuated more than the other ion concentrations. The increasing trend of  $\text{H}_2\text{S}$  concentrations with depth was not as pronounced. The only real exception was  $\text{Ca}^{2+}$  which displayed strong fluctuations in concentration throughout the core without a trend.

In order to calculate the relative abundances of the ions in the porewater of Lake Logipi, the average concentrations of the single anions and cations of the whole core were taken. The most abundant ions were  $\text{Cl}^-$  and  $\text{Na}^+$  representing 87.8 % of the anions and 98.0 % of the cations, respectively. Other important constituents were  $\text{SO}_4^{2-}$  (6.6 % of anions) and  $\text{F}^-$  (5.0 % of anions). Minor components were  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Br}^-$ , and  $\text{PO}_4^{3-}$  with 1.2 % or less.

#### *Reduced sulphur species*

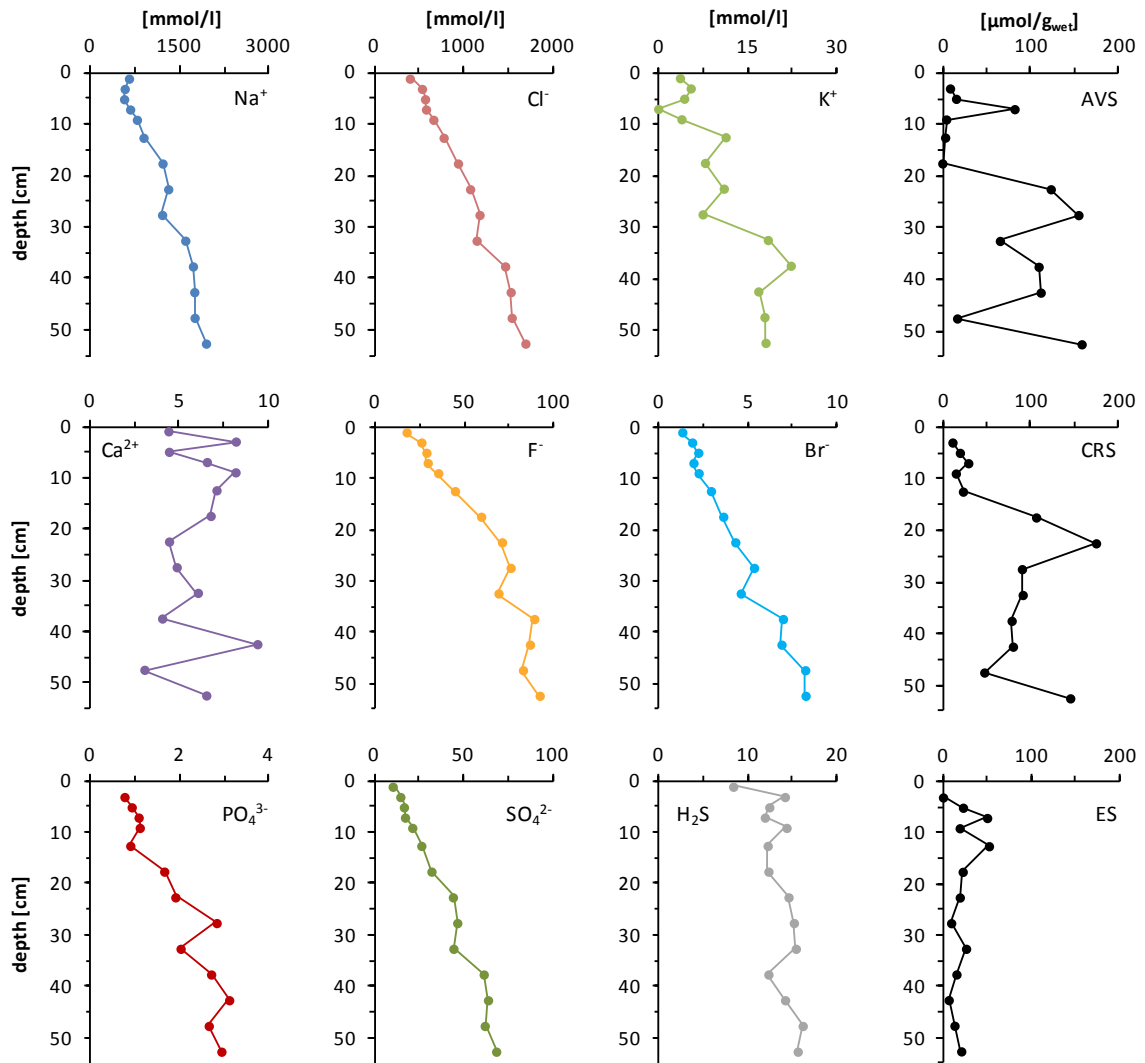
In the sediment core of Lake Logipi, the upper 15 cm were dominated by ES whereas the remaining part of the core was dominated by acid-volatile sulphur (AVS) and chromium-reducible sulphur (CRS; see fig. 3.2). AVS and CRS concentrations were within the same range and were about three times higher than ES concentrations.

### 3.2.B. Key characteristics

#### *Porewater profile*

Hypersaline Lake Logipi is mainly fed by hot springs located at the northern shore of the lake, where the cores for this study were taken (see fig. 1.6). Those hot springs might be the reason for the characteristic depth profiles of the ions (fig. 3.2): Saline hydrothermal water migrates upwards and mixes with less saline lake water seeping into the sediment. Calcium behaves differently and an explanation is attempted in subchapter 4.1.A.

High concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (1 390 mg/l and 1.45 mg/l, respectively) were reported in the lake's water and were explained by high bacterial activity which is further enhanced by



**Fig. 3.2:** Results of the porewater analysis and reduced sulphur species of Lake Logipi. For Ca<sup>2+</sup> see subchapter 4.1.A.

flamingo excrements (Castanier et al., 1993). Neither NH<sub>4</sub><sup>+</sup> nor NO<sub>3</sub><sup>-</sup> was detected in the sediment's porewater in this study, probably because bacterial activity in the lake is so high that nothing seeps into the sediment, but is instead utilised in the water column.

#### *Horizons of elemental sulphur as climate markers?*

A desiccation or near-desiccation of the lake is indicated by two ES horizons in 5 cm and 9 cm below the lake floor (b.l.f.; fig. 3.2). Those ES horizons may have been formed by sulphide-oxidising bacteria like *Beggiatoa* which are large, colourless sulphur bacteria found in various environments with varying salinities at the oxic-anoxic interface of sediments or microbial mats. *Beggiatoa* oxidises H<sub>2</sub>S under oxic conditions to ES which is stored as intracellular sulphur droplets (Schmidt et al., 1987; Hinck et al., 2007). Under anoxic conditions *Beggiatoa* can use stored NO<sub>3</sub><sup>-</sup> reserves as electron acceptors to oxidise the H<sub>2</sub>S (Hinck et al., 2007) or reduce the

internal ES to sulphide (Schmidt et al., 1987). Hints for the presence of *Beggiatoa* were found in form of filaments in the upper layers of the sediment analysed under the microscope.

During low lake levels, the currently anoxic lake bottom might have received enough oxygen for the sulphide-oxidising *Beggiatoa* populations to increase. The internally stored ES was left behind when lake levels again increased, leading again to anoxic lake-bottom conditions. That way, the two ES peaks in the sediment column would point to times of very low lake levels. Below approximately 15 cm b.l.f., ES concentrations are much lower and AVS and CRS are the dominant reduced sulphur species which are almost absent in the upper part of the core. That might point to lake levels which were on average higher than today, so that consequently conditions were permanently anoxic in the upper sediment and no large *Beggiatoa* communities could develop. The more permanent anoxic conditions at the lake bottom during that time favoured sulphate reduction and, consequently, the formation of iron sulphides.

### 3.3. Lake Eight

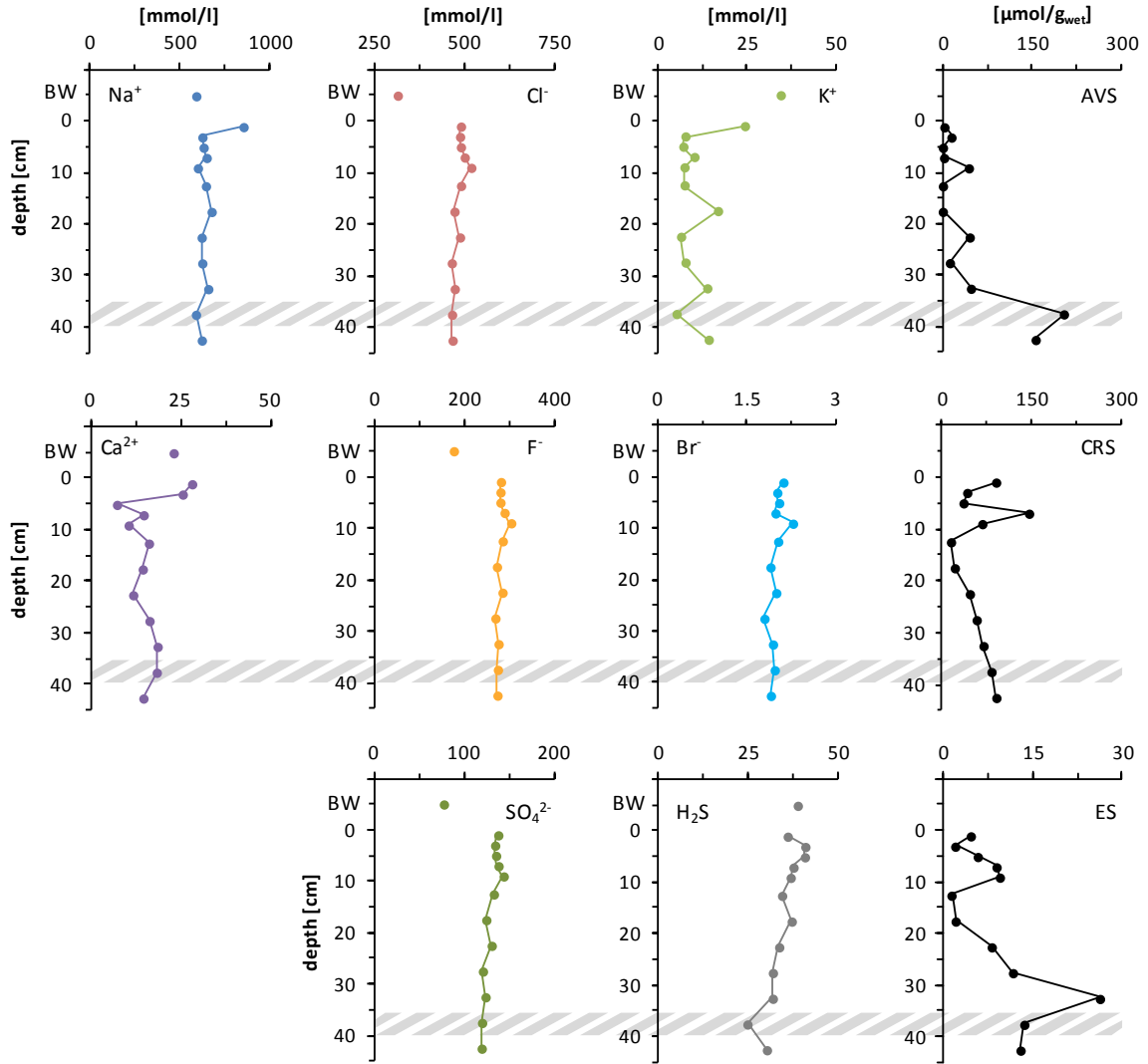
#### 3.3.A. Results

##### *Lake and porewater chemistry*

In Lake Eight, the hydrochemical properties of the lake's bottom and surface water were similar. The average conductivity of the lake water was 55 300  $\mu\text{S}/\text{cm}$ . Salinity of the surface water was slightly lower (44 g/l) than in the bottom water (50 g/l). The pH values were 9.9 for the surface water and 9.6 for the bottom water.

Dissolved ions found in the sediment porewater of Lake Eight included  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ , and  $\text{SO}_4^{2-}$  (see depth profiles in fig. 3.3).  $\text{H}_2\text{S}$  was also found. The depth profiles of all dissolved ions and  $\text{H}_2\text{S}$  looked similar with constant or decreasing concentrations with depth and significantly lower values in the bottom water of the lake. Cation concentrations in the uppermost porewater sample were significantly higher than in all other porewater samples.  $\text{K}^+$  concentrations were fluctuating throughout the core and the concentration in the bottom water was higher than in the underlying sediment.

In order to calculate the relative abundances of the ions in the porewater of Lake Eight, the average concentrations of the single anions and cations of the whole core were taken. The most abundant ions were  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$  representing 88.9 % of the anions and 93.3 % of the cations, respectively. Other important constituents were  $\text{F}^-$  (10.9 % of anions) and  $\text{Ca}^{2+}$  (4.9 % of cations). Minor components were  $\text{K}^+$  and  $\text{Br}^-$  with 1.8 % or less.



**Fig. 3.3:** Results of the porewater analysis and reduced sulphur species of Lake Eight. The grey layer located between 35 cm and 40 cm shows the position of the assumed desiccation horizon of the early 19th century drought. BW: bottom water. For Ca<sup>2+</sup> see subchapter 4.1.A.

### Reduced sulphur species

In the sediment core of Lake Eight, AVS had its highest concentrations in the two bottom samples, where a desiccation horizon is suspected (see fig. 3.3). CRS concentrations showed an increasing trend with depth and a distinct peak in 9 cm b.l.f. ES concentrations were even stronger increasing with depth and the highest concentrations were determined just above the assumed desiccation horizon. CRS was the most dominant TRIS compound when the desiccation horizon was excluded.

### Sedimentological characteristics

In 35 cm to 40 cm b.l.f., a black and stiff layer was evident (see fig. 3.3), which is assumed to be the desiccation horizon of the early 19th century drought.

### 3.3.B. Key characteristics

#### *Lake and porewater*

The lake and porewater of Lake Eight was dominated by  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  and also included a significant amount of  $\text{F}^-$ , which is expected from a lake in the Kenyan Rift Valley (Nanyaro et al., 1984; Dunkley et al., 1993).

The lake water is stratified due to slightly more saline bottom water. That stratification is probably not permanent, since the lake is likely well-mixed due to its size (200 m long, 100 m wide; Dunkley et al., 1993) and shallow depth of just a few meters.

#### *Detection of a desiccation horizon?*

A severe drought in East Africa, which reached its climax around 1820 to 1830 (Nicholson, 1998), is evident in all affected lake sediments (Nicholson, 1998; Verschuren, 1999a; Bessems et al., 2008; De Cort et al., 2013). Some lake beds stood dry so that older lake sediments were oxidised and compacted to form stiff and low-organic desiccation horizons (e.g. in Lake Naivasha and its satellites; Verschuren, 1999a; Bessems et al., 2008).

Comparison between the sediment core of this study and the age profile for that lake (Junginger et al., in prep.) shows that the layer directly above the proposed desiccation horizon (see dashed layer in fig. 3.3) dates back to the year 1879 ( $\pm 30$  years). This fits relatively well with the onset of lake transgressions in other parts of East Africa around 1850 (e.g. Lakes Turkana, Naivasha, Malawi; Nicholson, 1998).

The concentration of AVS was significantly higher in the desiccation horizon than in the rest of the core which is probably due to compaction. The high ES concentrations directly above the horizon likely represent the stage of lake filling, when the lake level was low enough to allow a large population of sulphide oxidisers to grow (see subchapter 3.2.B).

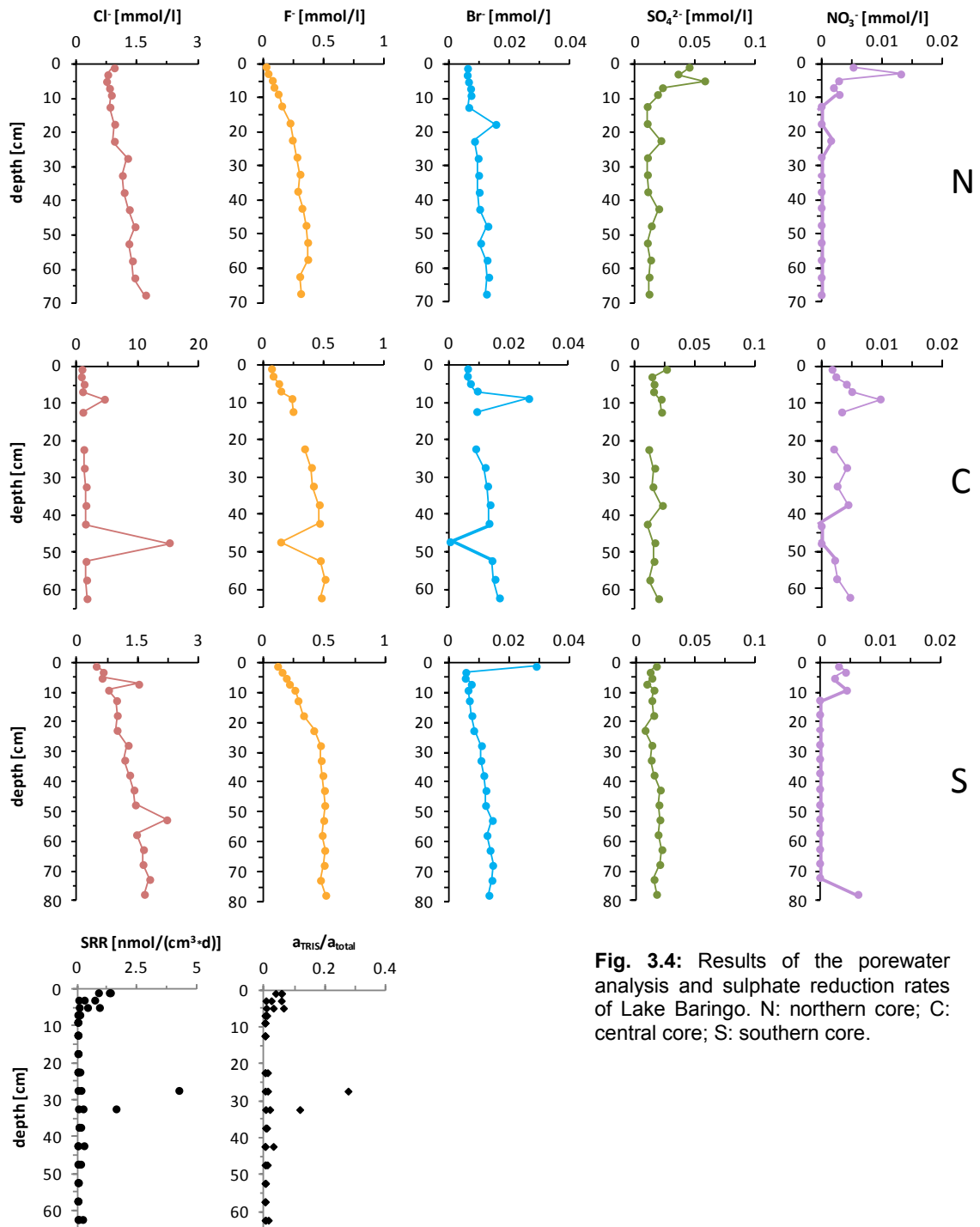
## 3.4. Lake Baringo

### 3.4.A. Results

#### *Lake and porewater chemistry*

In Lake Baringo, conductivity and pH of the lake's surface water were the same at all three sites with 450  $\mu\text{S}/\text{cm}$  and 8.0, respectively.

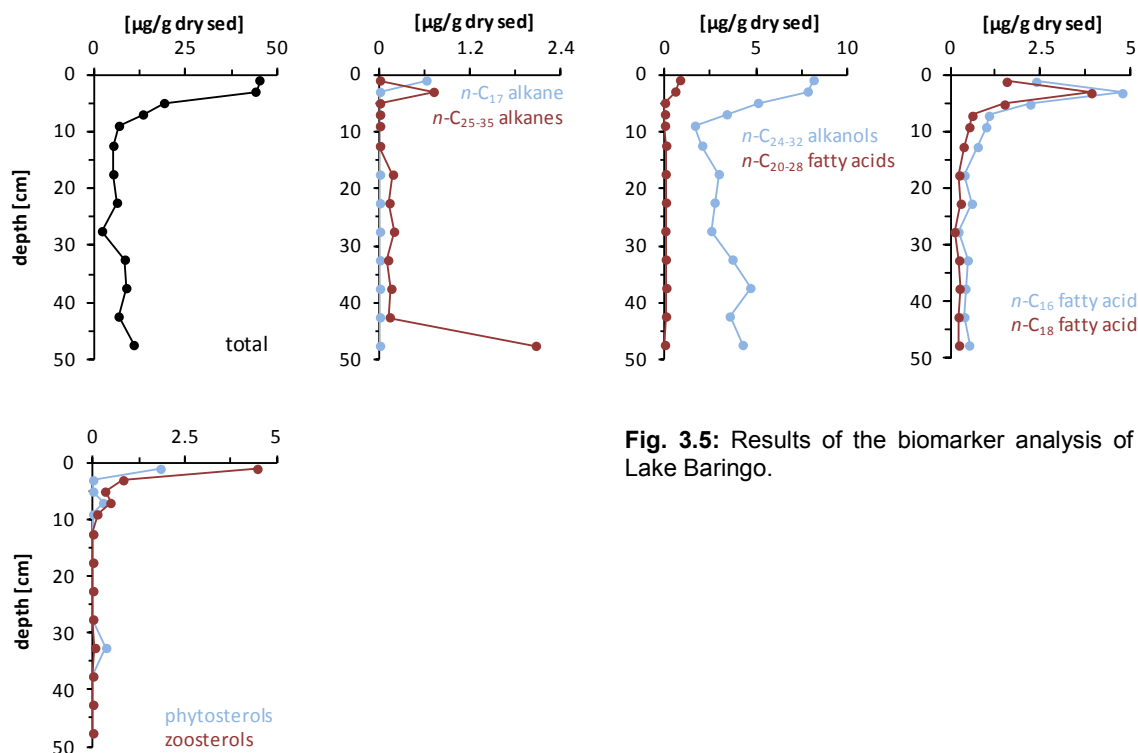
Dissolved anions found in the sediment porewater of Lake Baringo included  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  (see depth profiles in fig. 3.4).  $\text{H}_2\text{S}$  concentrations were below the detection limit. The depth profiles of  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{Br}^-$  showed the same increasing trends with depth, but with unique



**Fig. 3.4:** Results of the porewater analysis and sulphate reduction rates of Lake Baringo. N: northern core; C: central core; S: southern core.

distinct peaks.  $\text{SO}_4^{2-}$  concentrations showed only minor variations, whereas  $\text{NO}_3^-$  behaved differently at every site.

In order to calculate the relative abundances of the ions in the porewater of Lake Baringo, the average concentrations of the single anions of the whole core were taken. The most abundant anion was  $\text{Cl}^-$  representing 74.5 % to 87.1 % of the anions depending on the location. Another important constituent was  $\text{F}^-$  ranging between 11.2 % and 22.9 %. Minor compounds were  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Br}^-$  with 2.9 % or less.



**Fig. 3.5:** Results of the biomarker analysis of Lake Baringo.

#### *Sulphate reduction rates*

Sulphate reduction rates (SRR) in the sediment core of Lake Baringo showed a decreasing trend from 1.36 nmol/(cm<sup>3</sup> × d) in the uppermost sample to 0.08 nmol/(cm<sup>3</sup> × d) in 9 cm (see fig. 3.4). Values remained constant throughout the rest of the sediment core with the exception of two outliers in 27.5 cm and 32.5 cm, where SRR reached 4.21 nmol/(cm<sup>3</sup> × d) and 1.59 nmol/(cm<sup>3</sup> × d), respectively.

The ratio  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  was low throughout the core with maximum values of 0.06 found in the upper 7 cm. There were two outliers with higher values (0.27 and 0.14) in 27.5 cm and 32.5 cm depth.

#### *Organic geochemistry*

The important biomarkers found in Lake Baringo are listed in table 3.1 and the respective diagrams are shown in figure 3.5.

The total biomarker concentration in the sediment core of Lake Baringo was highest in the two uppermost samples reaching 45 µg/g<sub>dry wt.</sub>. Below those two samples, the concentration dropped to 7 µg/g<sub>dry wt.</sub> in 9 cm b.l.f. and stayed constant throughout the rest of the core. All biomarkers showed highest concentrations directly below the sediment surface, except carboxylate esters which were only present below 17.5 cm. Long-chain *n*-alkanes reached their highest concentration in the lowermost sample in 47.5 cm b.l.f.

**Table 3.1:** The table shows the important biomarkers found in Lake Baringo. n.a. = not attributed.

group	biomarker	origin
<i>n</i> -alkanes	<i>n</i> -C <sub>17</sub>	algae
	<i>n</i> -C <sub>25</sub> – <i>n</i> -C <sub>35</sub> ( <i>long-chain n-alkanes</i> )	higher plants
<i>n</i> -alkanols	<i>n</i> -C <sub>24</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-alkanols</i> )	higher plants
saturated <i>n</i> -fatty acids	<i>n</i> -C <sub>16</sub> & <i>n</i> -C <sub>18</sub>	various
	<i>n</i> -C <sub>20</sub> – <i>n</i> -C <sub>28</sub> ( <i>long-chain n-fatty acids</i> )	higher plants
phytosterols	(3β)-stigmast-5-en-3-ol ( <i>β-sitosterol</i> )	n.a.
	(3β,5α)-stigmastan-3-ol	n.a.
	(3β,22E,24R/S)-stigmasta-5,22-dien-3-ol ( <i>stigmasterol</i> )	n.a.
zoosterols	(3β,5α)-cholestan-3-ol	n.a.
	(3β)-cholest-5-en-3-ol ( <i>cholesterol</i> )	n.a.

### 3.4.B. Key characteristics

#### *Porewater profile*

The porewater profiles of the three locations in Lake Baringo did not differ regarding the general trends or the concentration ranges of the single anions (see fig. 3.4). The profiles of Cl<sup>-</sup>, F<sup>-</sup>, and Br<sup>-</sup> in the central core as well as the Cl<sup>-</sup> profile in the southern core showed unique peaks in each of the three cores. The Cl<sup>-</sup> peaks in the central and southern core might have the same age since the sedimentation rates in the south are higher due to several inflowing rivers (e.g. Perkerra). At the central site, degassing structures were observed in the depth with highest Cl<sup>-</sup> concentrations (47.5 cm). So this large Cl<sup>-</sup> peak might be the origin of a hydrothermal vent seeping into the lake. The negative excursions of F<sup>-</sup> and Br<sup>-</sup> in the central core are best explained by analytical inaccuracy since the detected amounts were in general very low.

#### *Sulphate reduction*

Sulphate reduction rates in the surface sediments of Lake Baringo were similar to other freshwater lakes (0.5 – 13 nmol/(cm<sup>3</sup> × d); Foti et al., 2007 and studies cited therein). Despite sulphate reduction, NO<sub>3</sub><sup>-</sup> was detected in the sediment's porewater, albeit in very low concentrations. In experimental studies on anaerobic sewer biofilms, it was shown that the presence of NO<sub>3</sub><sup>-</sup> does not affect the sulphate-reducing community in terms of cell numbers or sulphate-reducing activity (Mohanakrishnan et al., 2009).

Excluding the two outliers in 27.5 cm and 32.5 cm b.l.f., the a<sub>TRIS</sub>/a<sub>TOTAL</sub> ratio was generally low (max. 0.05) which shows that SO<sub>4</sub><sup>2-</sup> is not limiting sulphate reduction. For the two outliers, the



ratios exceed the accepted value of 0.1 and therefore, the respective SRR are not reliable (see also subchapter 2.3.B).

#### *Organic geochemistry*

The high sediment input, mainly due to overgrazing and deforestation, of  $10 \times 10^6$  t/a into Lake Baringo (Odada et al., 2005) causes a strong dilution of the organic material transported into the lake. That is why the total biomarker concentration in the sediment column of Lake Baringo was the lowest of all lakes studied ( $45 \mu\text{g/g}_{\text{dry wt.}}$  in the top sample). The available sample amounts were consequently not enough for a thorough analysis, especially for the fractions F 1 and F 2. Straight-chain compounds were attributed due to their common occurrence in higher plants and algae, respectively. It was impossible to attribute the sterols safely to certain origins, because of their low concentrations and their sporadic occurrence within the core.

### **3.5. Lake Bogoria**

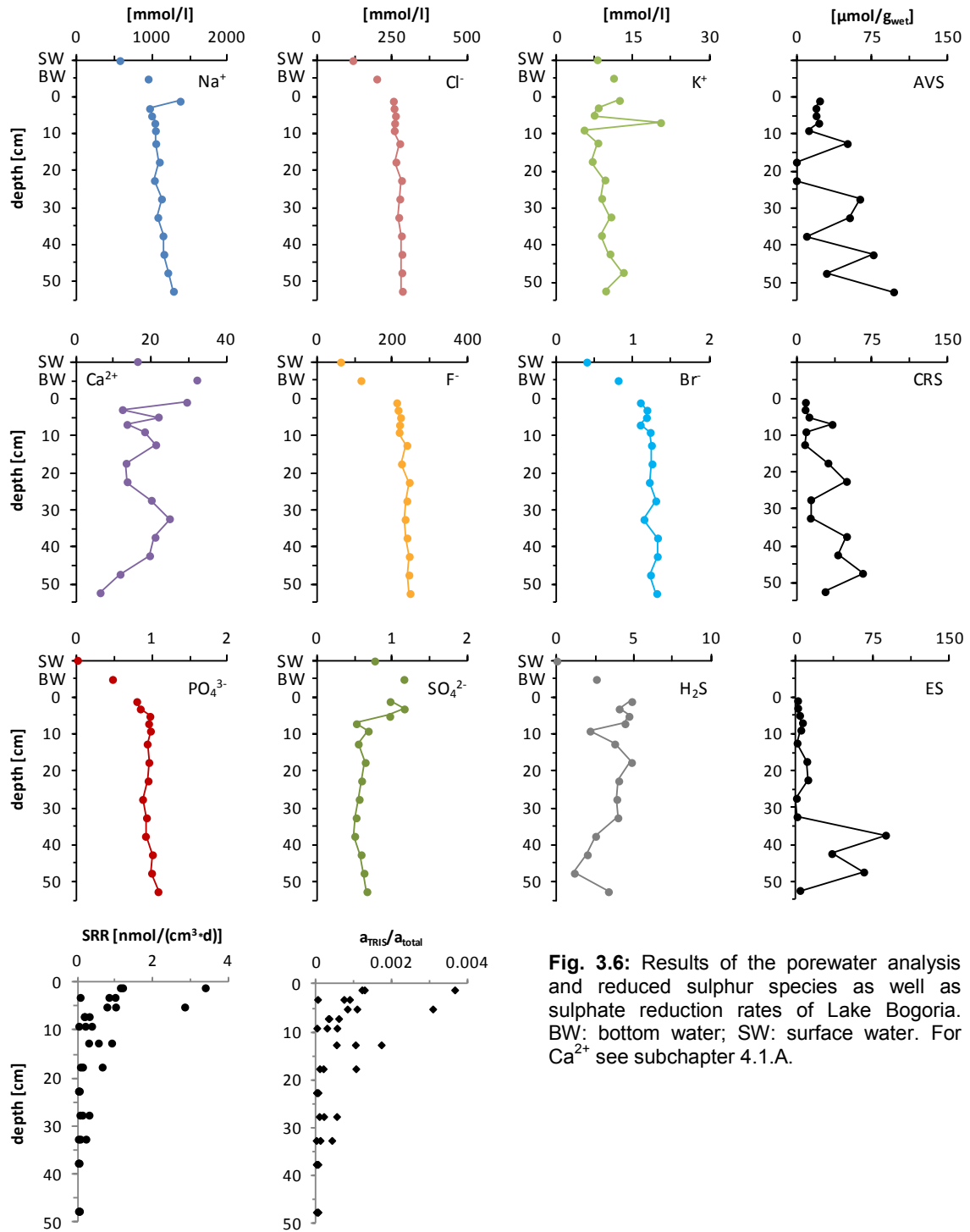
#### **3.5.A. Results**

##### *Lake and porewater chemistry*

In Lake Bogoria, bottom and surface water showed strong differences in their hydrochemical properties. Conductivity and salinity of the surface water were  $41\,000 \mu\text{S/cm}$  and  $40 \text{ g/l}$ , respectively. In the bottom water those values were significantly higher with  $61\,000 \mu\text{S/cm}$  for the conductivity and  $70 \text{ g/l}$  for the salinity. The pH values of the bottom and surface water were similar with 10.0 for the surface and 9.8 for the bottom water.

Dissolved ions found in the sediment porewater of Lake Bogoria included  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  (see depth profiles in fig. 3.6).  $\text{H}_2\text{S}$  was also found. Most ion concentrations in Lake Bogoria showed similar distribution patterns, with stable or slightly decreasing trends towards the top and less saline lake water.  $\text{K}^+$  and  $\text{SO}_4^{2-}$  concentrations both showed a distinct peak in 7 cm and 3 cm depth, respectively, but otherwise followed the general trend. The concentration of  $\text{Ca}^{2+}$ , on the other hand, showed stronger fluctuations. In contrast to other ions that were quantified,  $\text{H}_2\text{S}$  concentrations decreased with depth. It was also found in the bottom water of the lake.

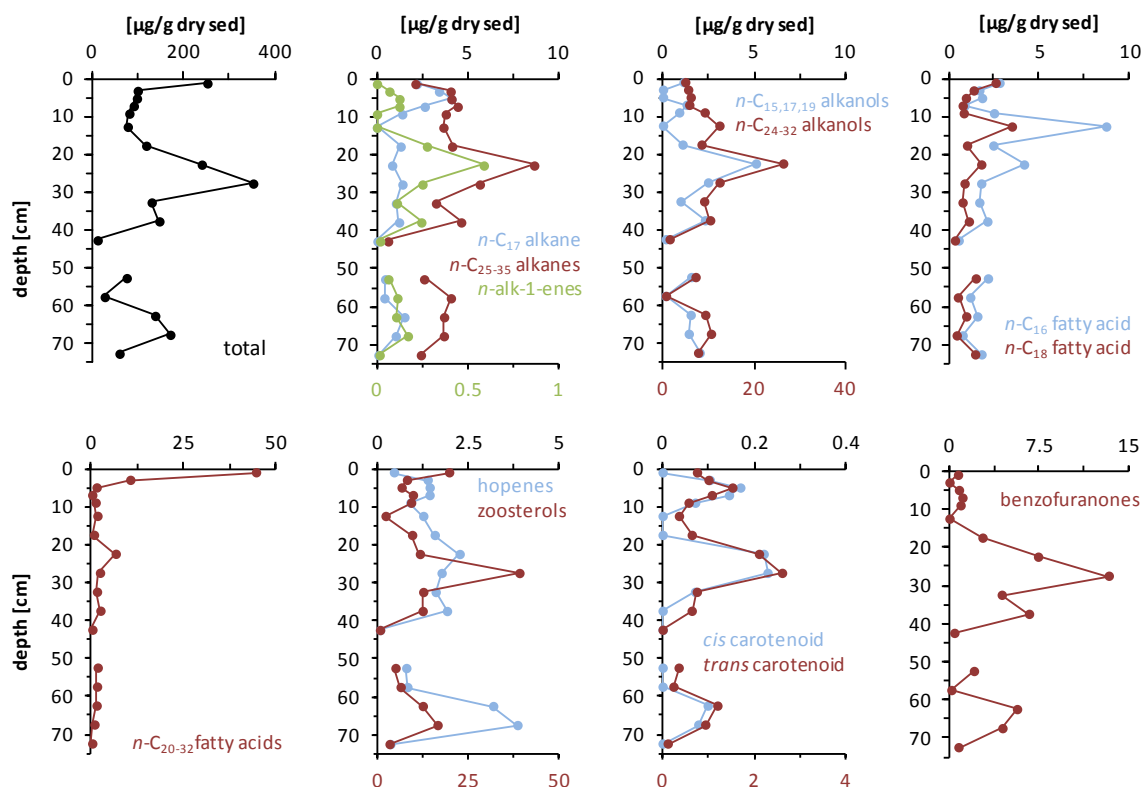
In order to calculate the relative abundances of the ions in the porewater of Lake Bogoria, the average concentrations of the single anions and cations of the whole core were taken. The most abundant ions were  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{Na}^+$  representing 99.1 % of the anions and 95.7 % of the cations, respectively. Another important compound was  $\text{Ca}^{2+}$  comprising 3.4 % of all cations. Minor components were  $\text{K}^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Br}^-$  with 0.9 % or less.



**Fig. 3.6:** Results of the porewater analysis and reduced sulphur species as well as sulphate reduction rates of Lake Bogoria. BW: bottom water; SW: surface water. For Ca<sup>2+</sup> see subchapter 4.1.A.

### Reduced sulphur species and sulphate reduction rates

In the sediment core of Lake Bogoria, AVS and CRS concentrations were within the same range and showed strong variations throughout the core (see fig. 3.6). ES was mainly present in the lower part of the core (below 32.5 cm) and reached equally high values than AVS and CRS.



**Fig. 3.7:** Results of the biomarker analysis of Lake Bogoria.

Sulphate reduction rates in the sediment core of Lake Bogoria showed a decreasing trend from 3.4 nmol/(cm<sup>3</sup> × d) in the uppermost sample to 0.01 nmol/(cm<sup>3</sup> × d) in 37.5 cm (see fig. 3.6). Values remained constant throughout the rest of the sediment core.

The ratio  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  was very low throughout the core with maximum values of 0.004 found in the uppermost sample.

#### Organic geochemistry

The important biomarkers found in Lake Bogoria are listed in table 3.2 and the respective diagrams are shown in figure 3.7.

The total biomarker concentration in the sediment core of Lake Bogoria showed strong fluctuations throughout the whole core. The concentrations varied between 10 µg/g<sub>dry wt.</sub> in 42.5 cm and 350 µg/g<sub>dry wt.</sub> in 27.5 cm. Most of the biomarkers followed that trend (i.e. long-chain *n*-alkanes, *n*-alk-1-enes, zoosterols). Other biomarkers (i.e. *n*-alkanols, unsaturated *n*-fatty acids, carotenoids, and benzofuranones) followed that trend below a depth of 10 cm, but above that no synchronicity was present anymore. Hopenes and the *n*-C<sub>17</sub> alkane showed the same trend as the other biomarker groups below 37.5 cm b.l.f.; above that, the concentration of hopenes stayed relatively constant, whereas the *n*-C<sub>17</sub> alkane concentration increased above

**Table 3.2:** The table shows the important biomarkers found in Lake Bogoria. n.a. = not attributed.

group	biomarker	origin
<i>n</i> -alkanes	<i>n</i> -C <sub>17</sub> <i>n</i> -C <sub>25</sub> – <i>n</i> -C <sub>35</sub> ( <i>long-chain n-alkanes</i> )	algae higher plants
<i>n</i> -alk-1-enes	<i>n</i> -C <sub>27</sub> – <i>n</i> -C <sub>29</sub>	higher plants
<i>n</i> -alkanols	<i>n</i> -C <sub>15</sub> ; <i>n</i> -C <sub>17</sub> ; <i>n</i> -C <sub>19</sub> ( <i>short-chain n-alkanols</i> ) <i>n</i> -C <sub>24</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-alkanols</i> )	n.a. higher plants
saturated <i>n</i> -fatty acids	<i>n</i> -C <sub>16</sub> & <i>n</i> -C <sub>18</sub> ( <i>short-chain n-fatty acids</i> ) <i>n</i> -C <sub>20</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-fatty acids</i> )	various higher plants
hopenes	hop-22(29)-ene II & III hop-17(21)-ene I hop-21-ene I	bacteria bacteria bacteria
zoosterols	(3β,5α)-cholestan-3-ol (3β,5β)-cholestan-3-ol (3α,5β)-cholestan-3-ol	algae mammals mammals?
carotenoids	4,5-didehydro-5,6,7,7',8,8',9,9',10,10',11,11',12,12',13,13',14,14'-octadecahydro-β,β-carotene ( <i>cis</i> & <i>trans</i> isomers)	cyanobacteria
benzofuranones	6-hydroxy-4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1-benzofuran-2(4H)-one ( <i>loliolide</i> ) 4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1-benzofuran-2(4H)-one ( <i>dihydroactinidiolide</i> )	xanthophylls carotenes

12.5 cm. Long-chain *n*-fatty acids showed a strong enrichment in the upper centimetres, whereas they followed the general zigzag trend below that depth. The two saturated short-chain fatty acids *n*-C<sub>16</sub> and *n*-C<sub>18</sub> showed minor fluctuations throughout the core, but had a major peak in 12.5 cm b.l.f.

### 3.5.B. Key characteristics

#### *Lake and porewater*

Lake Bogoria is an extremely saline and alkaline lake which is permanently stratified due to salinity differences of bottom and surface water (Harper et al., 2003). The quantified salinity of the bottom water was almost twice as high as that of the surface water (70 g/l and 40 g/l, respectively).

The ion profiles of the sediment core all showed constant or slightly increasing trends with depth, except Ca<sup>2+</sup> (see subchapter 4.1.A). The sediment contained a lot of gas, originating from methanogenic bacteria (De Cort et al., 2013), which disturbed the porewater significantly.

### *Methanogenesis vs. sulphate reduction*

Strong degassing of the sediment core observed during coring showed the important role of methanogenesis in the sediment of Lake Bogoria. Sulphate reduction, on the other hand, seems to predominate in the water column, because 1) SRR in the sediment were very low compared to the other saline lakes of the study (4 nmol/(cm<sup>3</sup> × d) instead of up to 800 nmol/(cm<sup>3</sup> × d)) and because 2) H<sub>2</sub>S was detected in the bottom water of the lake. The low  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  ratio shows that SO<sub>4</sub><sup>2-</sup> is not limiting sulphate reduction in the sediment.

Given that no sulphate reduction was detected below 20 cm b.l.f. and that SO<sub>4</sub><sup>2-</sup> concentrations of around 0.5 mmol/l in the porewater do not inhibit methanogenesis, it can be assumed that the boundary between sulphate reduction and methanogenesis is located in roughly 20 cm b.l.f.

### *Origin of n-alk-1-enes*

Long-chain *n*-alk-1-enes, like those found in Lake Bogoria (see table 3.2), are commonly found in higher plants (Kolattukudy, 1970; Matsumoto et al., 1990). The correlation of *n*-alk-1-ene and long-chain *n*-alkane concentrations ( $r^2 \sim 0.70$ ) additionally supports the terrestrial origin of those *n*-alk-1-enes.

### *Lake Bogoria as a climate record?*

Some biomarkers and reduced sulphur species in the sediment of Lake Bogoria showed similar fluctuations which might reflect changes in environmental conditions. The sediment core of this study covers roughly the time frame from the end of the 19th century drought to the present (see De Cort et al., 2013 for depth-age profile). Unlike other rift lakes, Lake Bogoria did not fall dry during the drought, although sedimentological data showed that the lake level dropped significantly around 1800 (De Cort et al., 2013). In the following, an attempt is made to correlate fluctuations of reduced sulphur species and biomarkers in the sediment core with lake-level changes reconstructed by De Cort et al. (2013).

Terrestrial biomarkers, short-chain *n*-alkanols, benzofuranones, and carotenoids as well as the reduced-sulphur species CRS and ES showed synchronous fluctuations, whereas AVS showed an asynchronous behaviour (fig. 3.6 and 3.7).

During low lake levels when water mixing oxygenates the lake bed, iron- and sulphide-oxidising bacteria oxidise AVS to ES. Consequently, less ES is produced during high lake levels and AVS concentrations remain higher. The Fe<sup>2+</sup> released during the oxidation of AVS reacts with H<sub>2</sub>S and ES to CRS (see Berner, 1970 and Berner et al., 1985). This reaction explains the synchronous behaviour of CRS and ES. During the time period from the early 19th century to around 1970, when lake levels were generally low, concentrations of ES were especially high. CRS concentrations, on the other hand, did not show such a pronounced increase, although

sufficient  $\text{Fe}^{2+}$  had to be available. A possible explanation might be that  $\text{H}_2\text{S}$  concentrations were very low during this time which slowed the production of CRS.

The carotenoids and their degradation products were more abundant during low lake levels, because those molecules ultimately originate from salt-tolerant cyanobacteria (Hirschberg and Chamovitz, 1994; Killops and Killops, 2013) which are more abundant during low lake levels. Additionally, microbial oxidation and photo-oxidation of the carotenoids during low lake levels increases the amounts of benzofuranones (see subchapter 4.2.D).

Even small changes in lake-level fluctuations can cause significant changes in the surface area of Lake Bogoria (De Cort et al., 2013). De Cort et al. (2013) suggested that during low lake levels streams reach the centre of the lake to deposit minerals with terrestrial origins. That might also be applicable to the terrestrial biomarkers of this study as higher concentrations were detected during times of low lake levels.

In the study of De Cort et al. (2013), high lake levels were associated with high magnetic susceptibilities. Consequently, high biomarker, CRS, and ES concentrations were associated with high magnetic susceptibilities and vice versa. High AVS concentrations, on the other hand, are associated with low magnetic susceptibilities.

The preservation of biomarkers in Lake Bogoria is generally good due to anoxic conditions below the chemocline (4 m below the water surface in August 2001, 1 m in January 2003; De Cort et al., 2013), which slows degradation significantly. Changes in biomarker concentrations therefore reflect lake-level changes. But it is important to notice that not all biomarkers follow those changes, i.e. the  $n\text{-C}_{17}$  alkane, short-chain  $n$ -fatty acids, and hopenes. The  $n\text{-C}_{17}$  alkane does not follow the general trend because it is commonly produced by many types of algae, regardless of their salinity preferences. The short-chain  $n$ -fatty acids seem to be produced mainly by methanogenic bacteria present in the sediment (De Cort et al., 2013; own observation) and are therefore not reflecting lake-level changes. The hopene distribution is probably influenced by the high salinity and/or alkalinity of the lake water (see subchapter 4.2.B) and might therefore not reflect lake-level changes.

## **3.6 Lake Naivasha**

### **3.6.A. Results**

#### *Lake and porewater chemistry*

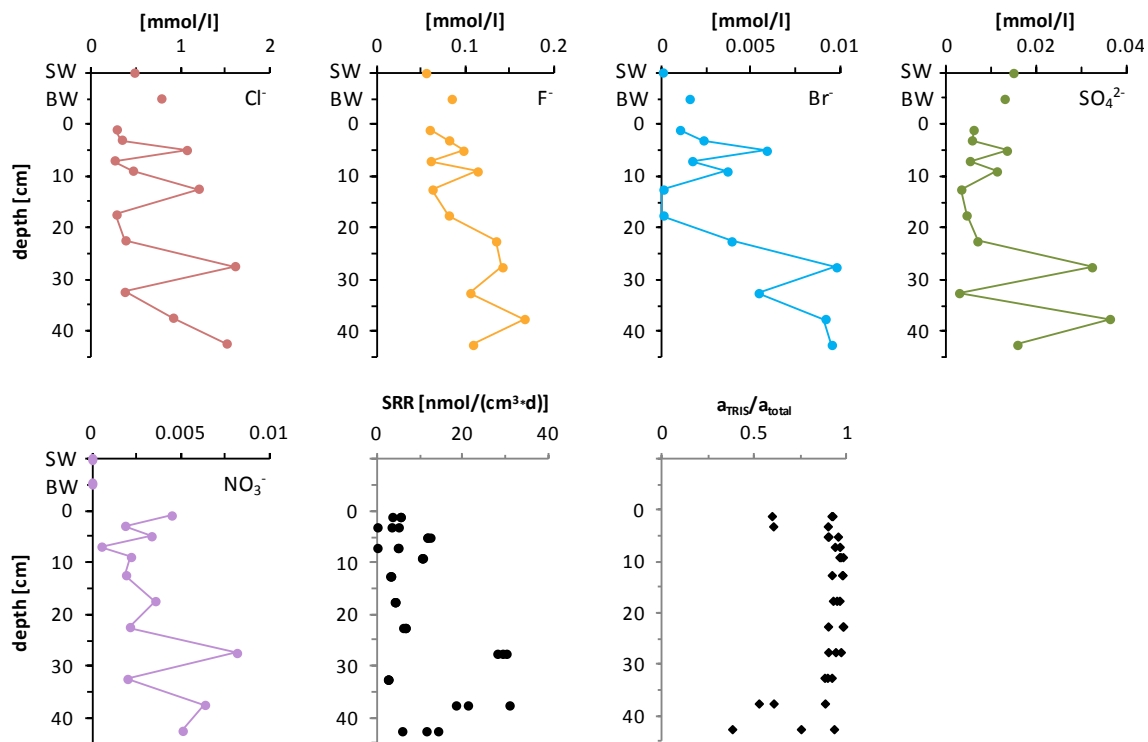
In Lake Naivasha, conductivity and salinity in the bottom water were higher than in the surface water of the lake. The averaged values were 232  $\mu\text{S}/\text{cm}$  for the conductivity and 2.3 g/l for the salinity. The pH value in the surface water (8.4) was considerably higher than in the bottom water (7.9).

Dissolved anions found in the sediment porewater of Lake Naivasha included  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  (see depth profiles in fig. 3.8).  $\text{H}_2\text{S}$  concentrations were below the detection limit. All anion concentrations showed a strong zigzag trend, with higher fluctuations in the lower part of the core (below 20 cm) and increasing concentrations with depth. Anion concentrations in the lake water fell into the range of the respective anions. No  $\text{NO}_3^-$  was detected in the lake water. In order to calculate the relative abundances of the ions in the porewater of Lake Naivasha, the average concentrations of the single anions of the whole core were taken. The most abundant anion was  $\text{Cl}^-$  representing 84.7 % of all anions. Other important constituents were  $\text{F}^-$  and  $\text{SO}_4^{2-}$  together comprising 14.6 % of all anions. Minor components were  $\text{Br}^-$  and  $\text{NO}_3^-$  with 0.6 % or less.

### Sulphate reduction rates

Sulphate reduction rates in the sediment core of Lake Naivasha showed a zigzag trend which followed the  $\text{SO}_4^{2-}$  content of the porewater (see fig. 3.8). The values varied between  $3.5 \text{ nmol}/(\text{cm}^3 \times \text{d})$  at the top and  $30.8 \text{ nmol}/(\text{cm}^3 \times \text{d})$  in the lower part of the core.

The ratio of  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  was almost 1 in the whole core. Lower values were only calculated at the top (upper 3 cm) and bottom of the core (below 37.5 cm).

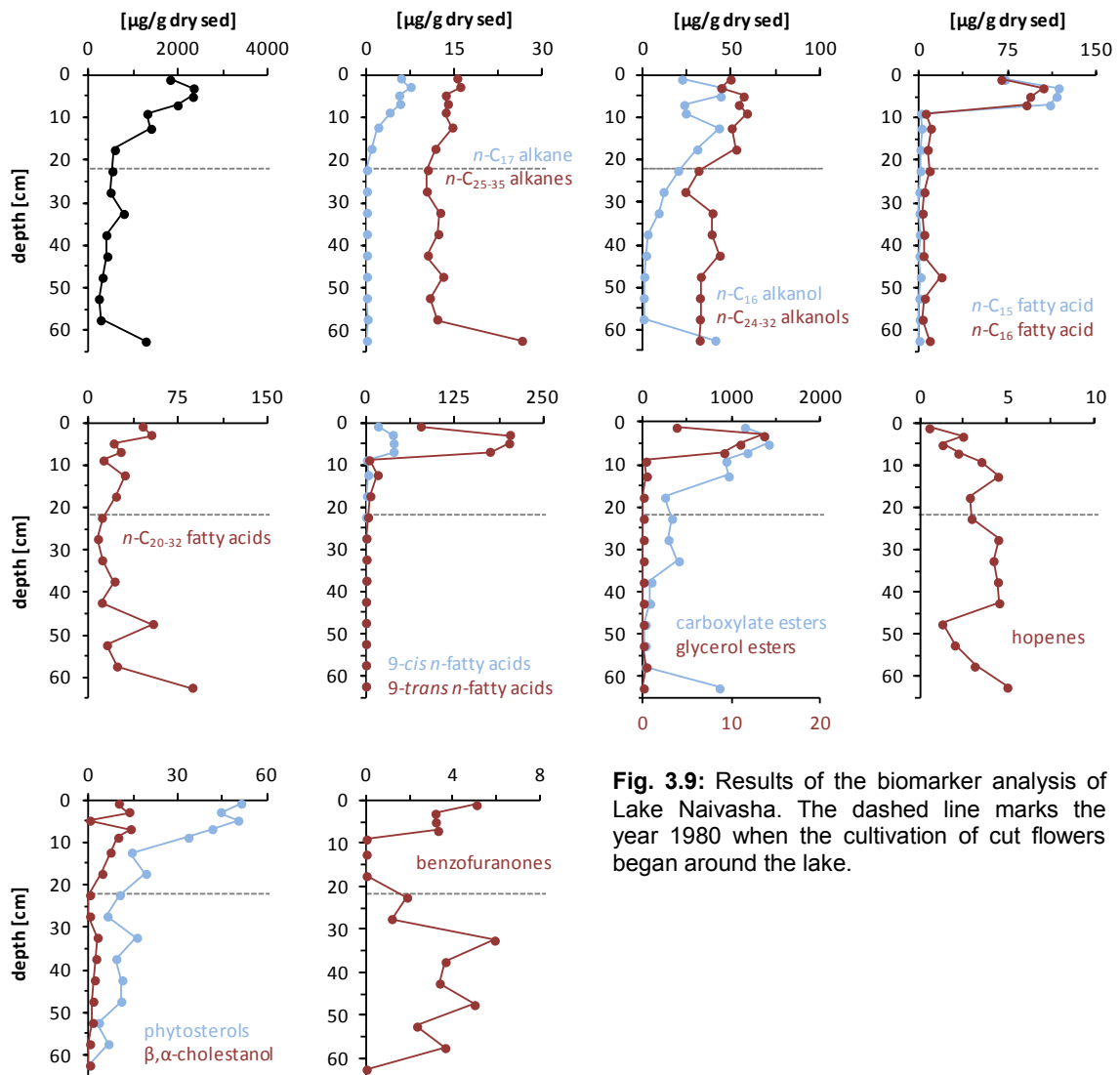


**Fig. 3.8:** Results of the porewater analysis and sulphate reduction rates of Lake Naivasha. BW: bottom water; SW: surface water.

### Organic geochemistry

The important biomarkers found in Lake Naivasha are listed in table 3.3 and the respective diagrams are shown in figure 3.9.

The total biomarker concentration in the sediment core of Lake Naivasha decreased from values of 2 330  $\mu\text{g/g}_{\text{dry wt.}}$  at the surface to 569  $\mu\text{g/g}_{\text{dry wt.}}$  in 17.5 cm b.l.f. Below that depth, the concentration decreased moderately and was higher in the lowermost sample with 1 260  $\mu\text{g/g}_{\text{dry wt.}}$ . Phytosterols, (3 $\beta$ ,5 $\alpha$ )-cholestan-3-ol, *n*-alkanes, *n*-alkanols, and carboxylate esters generally followed the same trend. Other biomarkers, namely saturated *n*-C<sub>15</sub> and *n*-C<sub>16</sub> fatty acids, unsaturated *n*-fatty acids as well as glycerol esters showed high concentrations in the upper 10 cm, whereas they were very low-concentrated in the remaining part of the core. Long-chain *n*-fatty acids, hopenes, and benzofuranones distributions fluctuated throughout the core.



**Fig. 3.9:** Results of the biomarker analysis of Lake Naivasha. The dashed line marks the year 1980 when the cultivation of cut flowers began around the lake.



**Table 3.3:** The table shows the important biomarkers found in Lake Naivasha. n.a. = not attributed.

group	biomarker	origin
<i>n</i> -alkanes	<i>n</i> -C <sub>17</sub> <i>n</i> -C <sub>25</sub> – <i>n</i> -C <sub>35</sub> ( <i>long-chain n-alkanes</i> )	algae higher plants
<i>n</i> -alkanols	<i>n</i> -C <sub>14</sub> – <i>n</i> -C <sub>18</sub> ( <i>short-chain n-alkanols</i> ) <i>n</i> -C <sub>24</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-alkanols</i> )	bacteria/algae higher plants
saturated <i>n</i> -fatty acids	<i>n</i> -C <sub>15</sub> & <i>n</i> -C <sub>16</sub> ( <i>short-chain n-fatty acids</i> ) <i>n</i> -C <sub>20</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-fatty acids</i> )	bacteria higher plants
unsaturated <i>n</i> -fatty acids	9- <i>trans n</i> -C <sub>12</sub> – <i>n</i> -C <sub>18</sub> 9- <i>cis n</i> -C <sub>14</sub> – <i>n</i> -C <sub>16</sub>	bacteria bacteria
hopenes	hop-22(29)-ene III hop-17(21)-ene I hop-21(22)-ene I	bacteria bacteria bacteria
phytosterols	(3β,24R)-ergost-5-en-3-ol ( <i>campesterol</i> ) (3β,5α,24R)-ergostan-3-ol ( <i>3β-campestanol</i> ) (3β,22E,24R/S)-stigmasta-5,22-dien-3-ol ( <i>stigmasterol</i> ) (3β)-stigmast-5-en-3-ol ( <i>β-sitosterol</i> ) (3β,5α)-stigmastan-3-ol	algae n.a. algae algae n.a.
zoosterols	(3β,5α)-cholestan-3-ol	algae
carboxylate esters	tetradecyl decanoate pentadecyl decanoate I & II pentadecyl dodecanoate I & II hexadecyl decanoate I & II hexadecyl undecanoate I & II & III hexadecyl dodecanoate I & II & III heptadecyl dodecanoate I & II & III octadecyl dodecanoate I & II & III	various various various various various various various various
glycerol ester	2,3-dihydroxypropyl pentadecanoate 2,3-dihydroxypropyl hexadecanoate	bacteria bacteria
benzofuranones	6-hydroxy-4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1-benzofuran-2(4H)-one ( <i>loliolide</i> ) 4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1-benzofuran-2(4H)-one ( <i>dihydroactinidiolide</i> )	xanthophylls carotenes

### 3.6.B. Key characteristics

#### *Porewater profile*

The anion profiles of Lake Naivasha all showed similar fluctuations throughout the sediment core (fig. 3.8), which lead to the assumption that they might be climate-related. It is not possible to prove that, because different water sources (e.g. lake water, hydrothermal vents), diffusion of ions, porewater mixing due to biological activity, and unregulated water extraction by farmers and the local population strongly influence the ion distributions. Using salinity for climate reconstruction is generally problematic, because the relationship between climate and salinity is indirect and complex due to salinity regulation via groundwater outflow and memory effects of the former hydrological history on the present salinity (Verschuren, 2003) as well as smoothing of the profiles by diffusion.

#### *Sulphate reduction*

Sulphate reduction rates fluctuated strongly within the sediment core and were generally higher between 10 cm and 35 cm (fig. 3.8). An  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  ratio of nearly 1 throughout the core shows that  $\text{SO}_4^{2-}$  is likely limiting sulphate reduction in the sediment. The ratio also shows that the turnover of  $\text{SO}_4^{2-}$  is very high and that the calculated SRR are not reliable. Despite the high turnover of  $\text{SO}_4^{2-}$ , no  $\text{H}_2\text{S}$  was detected in the porewater. An explanation for the absence of that molecule is the rapid precipitation of iron sulphides. Unfortunately, reduced sulphur species were not analysed in the sediment of Lake Naivasha.

#### *Origin of carboxylate esters and phytosterols*

Carboxylate esters were an important biomarker group in the sediment of Lake Naivasha comprising around 50 % of all biomarkers. Carboxylate esters are common in higher plants, but usually range between  $\text{C}_{38}$  and  $\text{C}_{50}$  in chain length (Rielley et al., 1991). The molecules found in the sediment of Lake Naivasha were shorter, only  $\text{C}_{24}$  to  $\text{C}_{30}$ . According to Rielley et al. (1991), there are two possible explanations for those short homologues: a microbial origin or condensation of *n*-alkanols with *n*-fatty acids in the sediment. Aquatic zooplankton is an additional possible source (Fukushima and Ishiwatari, 1984). The concentrations of carboxylate esters in this study correlated relatively well with the concentrations of the *n*- $\text{C}_{17}$  alkane ( $r^2 = 0.78$ ), short-chain *n*-alkanols ( $r^2 = 0.70$ ), and saturated, short-chain *n*-fatty acids ( $r^2 = 0.63$ ), suggesting a main input from algae and bacteria.

The phytosterols stigmasterol,  $\beta$ -sitosterol, and campesterol are usually characteristic for higher plants (Wen-Yen and Meinschein, 1976; Killops and Killops, 2013), but were also reported in algae (Nishimura and Koyama, 1976; Hassett and Lee, 1977; Volkman, 2003). Volkman (1986)

suggested a campesterol/stigmasterol/ $\beta$ -sitosterol ratio of 1 : 1.6 : 6.6 for higher plants and a lower ratio for algae to distinguish between the two groups. A ratio of 1 : 0.5 : 0.3 in the surface sample and a strong correlation with the  $n$ -C<sub>17</sub> alkane ( $r^2 \geq 0.78$ ) points to a mainly algal origin for those sterols in Lake Naivasha.

#### *Influence of floriculture*

The area around Lake Naivasha is intensely used to grow cut flowers, especially roses, which comprise around 70 % of all flowers grown around the lake (*Kenya Flower Council*). The Kenyan export of cut flowers increased exponentially from 10 946 t in 1988 to 136 601 t in 2014 (*Kenya Flower Council*).

The sediment core from Lake Naivasha was correlated with the age-depth profile of Stoof-Leichsenring et al. (2011), whose core was taken in close proximity to this study's coring position. Consequently, similar sedimentation rates for both cores can be assumed. Stoof-Leichsenring et al. (2011) determined sedimentation rates of 1 cm/a for the last 5 years of sedimentation (corresponding to the years 2002 to 2007 AD). For comparison with this study's sediment core, a constant sedimentation rate of 1 cm/a was assumed in order to correct for the additional sediment load of the last 5 years. That way, the year 1980 was located in 22.5 cm b.l.f., which fits very well with the onset of floriculture.

Since the early 1980s, when floriculture started around the lake, the total biomarker concentration increased exponentially and was the highest of all studied lakes (1 800  $\mu\text{g/g}_{\text{dry}}$  in the top sample; fig. 3.9). The same increase was observed for biomarkers characteristic for higher plants (i.e. long-chain  $n$ -alkanes,  $n$ -alkanols, and  $n$ -fatty acids) and algae (i.e.  $n$ -C<sub>17</sub> alkane and sterols). As a result, the growing floriculture around the lake is reflected in the increasing amounts of straight-chain compounds in the sediment. The analogous increase of algal biomarkers can be explained by the high amounts of fertilisers which reach the lake and promote algal growth (Mekonnen et al., 2012).

#### *Microbial activity*

High concentrations of saturated and unsaturated short-chain  $n$ -fatty acids (especially the saturated  $n$ -C<sub>15</sub> and the unsaturated  $n$ -C<sub>16</sub> and  $n$ -C<sub>18</sub>) as well as glycerol esters were detected in the upper 10 cm of the sediment core, but were rarely present below that depth (fig.3.9). Those biomarkers are all either directly produced by microbes (e.g. unsaturated  $n$ -fatty acids; Kawamura et al., 1987; Meyers and Ishiwatari, 1993) or are degradation products of other biomarkers (e.g. saturated  $n$ -fatty acids; Gaskell et al., 1976; Meyers and Ishiwatari, 1993). Previously reported elevated amounts of odd-numbered  $n$ -alkanols as an indicator for high bacterial activity (Seguel et al., 2001) additionally support microbial productivity (see also fig.

4.1). It is suggested that this zone consists of aerobes and anaerobes, because of the co-occurrence of observed bioturbations in the sediment and sulphate reduction.

Below that zone, in 10 cm to 35 cm b.l.f., SRR were even higher than in the sediment layers above (fig. 3.8), but bioturbations and the biomarkers for microbial activity were missing (fig. 3.9). Therefore, the bacterial community consists only of anaerobes.

Another explanation is that the high numbers of microbes commonly present at the sediment surface produce and degrade more organic matter than the smaller number of microbes in a lower depth, explaining why the characteristic biomarkers were only present in the upper 10 cm of the core.

### 3.7. Lake Oloiden

#### 3.7.A. Results

##### *Lake and porewater chemistry*

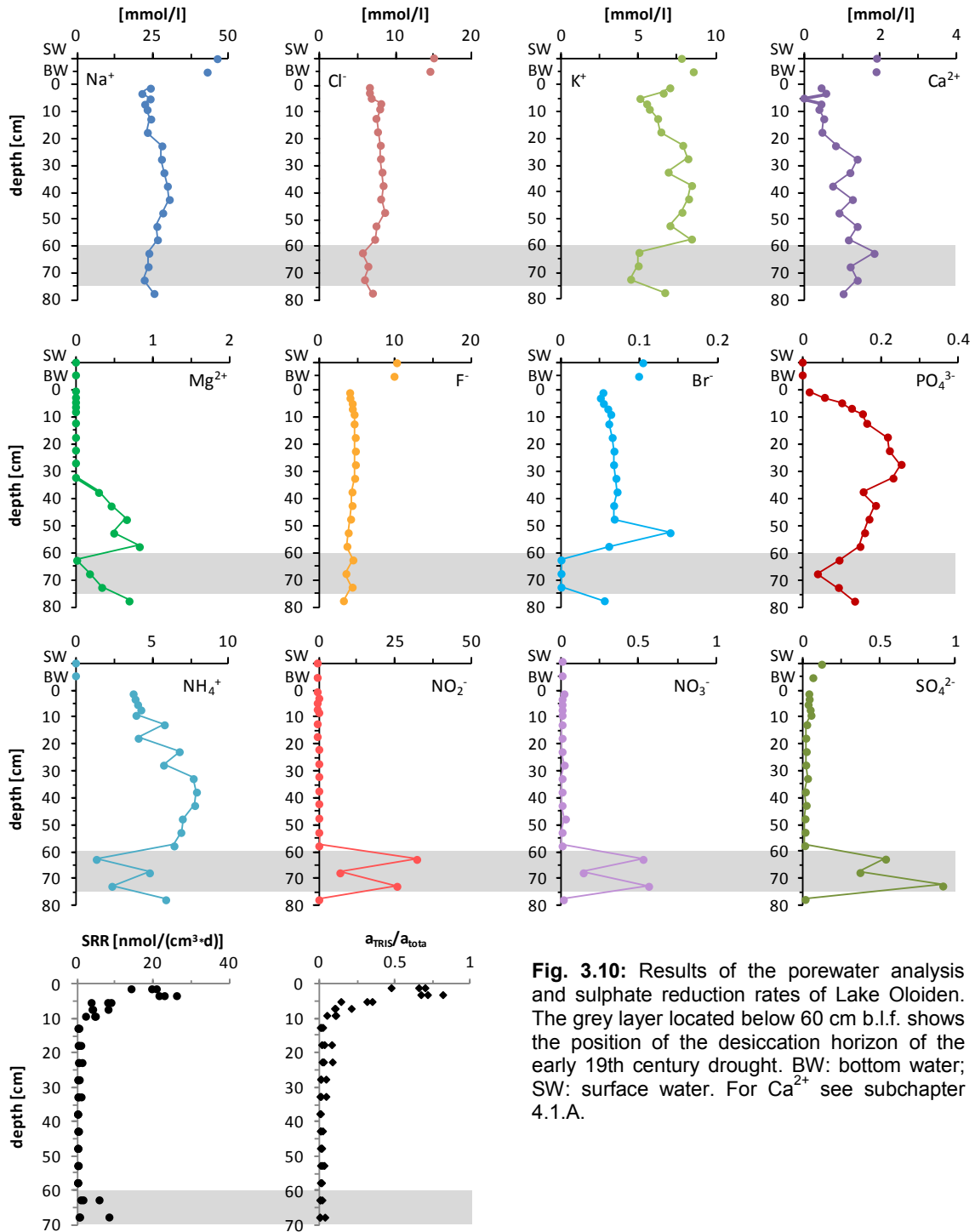
In Lake Oloiden, conductivity, salinity, and pH were similar in the bottom and surface water. The average values were 6 250  $\mu\text{S}/\text{cm}$  for conductivity, 6.0 g/l for salinity, and 9.8 for the pH.

Dissolved ions found in the sediment porewater of Lake Oloiden included  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  (see depth profile in fig. 3.10).  $\text{H}_2\text{S}$  concentrations were below the detection limit. Outside the desiccation horizon in 60 cm to 80 cm depth, the concentrations of all anions except  $\text{PO}_4^{3-}$  were constant. Cation concentrations showed more variations.  $\text{Mg}^{2+}$  was only detected below 32.5 cm. Within the desiccation horizon,  $\text{Mg}^{2+}$ ,  $\text{Br}^-$ , and  $\text{NH}_4^+$  concentrations were significantly lower;  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , on the other hand, were significantly higher concentrated than in the 'regular' sediment. In the lake water, the concentration of all ions was, in general, higher than in the underlying sediment core.

In order to calculate the relative abundances of the ions in the porewater of Lake Oloiden, the average concentrations of the single anions and cations of the whole core were taken. The most abundant ions were  $\text{Cl}^-$  and  $\text{Na}^+$  representing 49.0 % of the anions and 66 % of the cations, respectively. Other important constituents were  $\text{F}^-$  (28.8 % of anions),  $\text{NO}_2^-$  (18.6 % of anions),  $\text{K}^+$  (16.6 % of cations), and  $\text{NH}_4^+$  (11.8 % of cations). Minor components were  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$  with 4.8 % or less.

##### *Sulphate reduction rates*

Sulphate reduction rates in the sediment core of Lake Oloiden showed the characteristic hyperbolic curve (see fig. 3.10). The values showed a decreasing trend from 26  $\text{nmol}/(\text{cm}^3 \times \text{d})$



**Fig. 3.10:** Results of the porewater analysis and sulphate reduction rates of Lake Oloiden. The grey layer located below 60 cm b.l.f. shows the position of the desiccation horizon of the early 19th century drought. BW: bottom water; SW: surface water. For  $\text{Ca}^{2+}$  see subchapter 4.1.A.

in the uppermost sample to  $0.4 \text{ nmol}/(\text{cm}^3 \times \text{d})$  in 12.5 cm. Values remained constant throughout the rest of the core. In the desiccation horizon, SRR increased again to  $8.2 \text{ nmol}/(\text{cm}^3 \times \text{d})$ .

The ratio  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  also displayed a hyperbolic curve. The values decreased from 0.82 at the top to 0.4 in 27.5 cm and stayed constant below this depth.

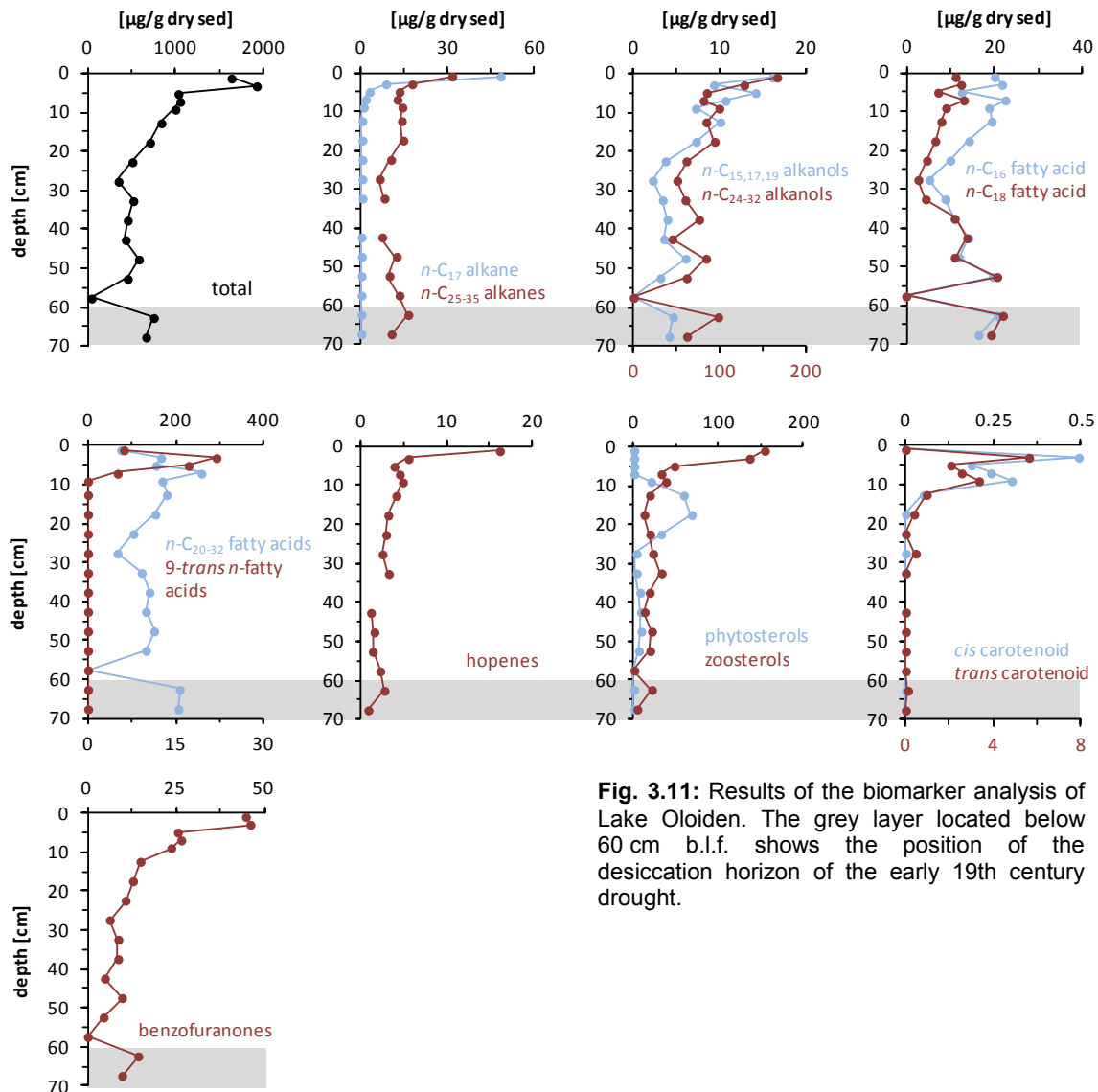
### Organic geochemistry

The important biomarkers found in Lake Oloiden are listed in table 3.4 and the respective diagrams are shown in figure 3.11.

The total biomarker concentration in the sediment core of Lake Oloiden was highest in 3 cm b.l.f. reaching 1 915 µg/g<sub>dry wt.</sub>. The concentration decreased to 40 µg/g<sub>dry wt.</sub> in 57.5 cm. The biomarker concentration in the desiccation horizon was higher, reaching 746 µg/g<sub>dry wt.</sub>. Most of the single biomarkers showed a similar trend, i.e. *n*-alkanes, long-chain *n*-alkanols, unsaturated *n*-fatty acids, hopenes, zoosterols, and benzofuranones. Saturated *n*-fatty acids just showed moderate concentration increases towards the top. Phytosterols were mainly found between 10 cm and 25 cm, whereas carotenoids were only found in the upper 10 cm of the sediment core. In the sample directly above the desiccation horizon, the majority of biomarkers was very low-concentrated.

**Table 3.4:** The table shows the important biomarkers found in Lake Oloiden. n.a. = not attributed.

group	biomarker	origin
<i>n</i> -alkanes	<i>n</i> -C <sub>17</sub> <i>n</i> -C <sub>25</sub> – <i>n</i> -C <sub>35</sub> ( <i>long-chain n-alkanes</i> )	algae higher plants
<i>n</i> -alkanols	<i>n</i> -C <sub>15</sub> ; <i>n</i> -C <sub>17</sub> ; <i>n</i> -C <sub>19</sub> ( <i>short-chain n-alkanols</i> ) <i>n</i> -C <sub>24</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-alkanols</i> )	n.a. higher plants
saturated <i>n</i> -fatty acids	<i>n</i> -C <sub>16</sub> & <i>n</i> -C <sub>18</sub> ( <i>short-chain n-fatty acids</i> ) <i>n</i> -C <sub>20</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-fatty acids</i> )	various higher plants
unsaturated <i>n</i> -fatty acids	9- <i>trans n</i> -C <sub>15</sub> , <i>n</i> -C <sub>16</sub> , <i>n</i> -C <sub>18</sub>	bacteria
hopenes	hop-22(29)-ene I & II & III, hop-17(21)-ene, hop-21(22)-ene I	bacteria
phytosterols	(3β,5α,24R)-ergostan-3-ol ( <i>β-campestanol</i> ) (3β,5α)-stigmastan-3-ol (3β,5α,22E)-stigmasta-7,22-dien-3-ol ( <i>α-spinosterol</i> )	<i>Salvinia</i> <i>Salvinia</i> <i>Salvinia</i>
zoosterols	(3β,5α)-cholestan-3-ol (3α,5β)-cholestan-3-ol (3β,5β)-cholestan-3-ol (3β)-cholest-5-en-3-ol ( <i>cholesterol</i> )	algae mammals? mammals plankton
carotenoids	4,5-didehydro-5,6,7,7',8,8',9,9',10,10',11,11',12,12',13,13', 14,14'-octadecahydro-β,β-carotene ( <i>cis</i> & <i>trans</i> isomers)	cyanobacteria
benzofuranones	6-hydroxy-4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1- benzofuran-2(4H)-one ( <i>loliolide</i> ) 4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1-benzofuran-2(4H)-one ( <i>dihydroactinidiolide</i> )	xanthophylls carotenes



**Fig. 3.11:** Results of the biomarker analysis of Lake Oloiden. The grey layer located below 60 cm b.l.f. shows the position of the desiccation horizon of the early 19th century drought.

### 3.7.B. Key characteristics

#### Porewater profile

Ion concentrations were much higher in the lake water of Lake Oloiden than in the underlying porewater (fig. 3.10). That is unusual, because the lake received, like all other rift lakes, more precipitation in recent years. The resulting desalination of the lake water observed in the other lakes of this study was expected to be smaller in Lake Oloiden, since the lake mainly receives new water through rainfall, through a narrow canal from Lake Naivasha (Verschuren, 1999a), and via groundwater flow from the main lake (Stoof-Leichsenring et al., 2011). The latter is a possible explanation for the less saline porewater of Lake Oloiden. Fresh groundwater from Lake Naivasha dilutes the porewater in the sediment of Lake Oloiden and additionally leads to a dilution of the lake's bottom water, which is slightly less saline than the surface water. Since the

shallow lake is well-mixed, the observed differences between bottom and surface water were only small.

#### *Sulphate reduction*

Although SRR were high in the sediment of Lake Oloiden, no H<sub>2</sub>S was detected. The sediment is rich in iron (Tarras-Walshberg, 1986; Mavuti and Harper, 2006) which might bind the released H<sub>2</sub>S immediately to form iron sulphides. Unfortunately, reduced sulphur species were not analysed in the sediment of Lake Oloiden.

The high ratios of  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  of up to 0.8 in the upper 10 cm b.l.f. show that SO<sub>4</sub><sup>2-</sup> turnover is too high and that the calculated SRR are not reliable. Below this depth, the low  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  ratios show that the data is more reliable, although SRR were in general also low. In the desiccation horizon, SO<sub>4</sub><sup>2-</sup> concentrations and SRR were both higher than in the overlying sediment. However, the very low  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  ratios of approximately 0.01 show that the turnover of SO<sub>4</sub><sup>2-</sup> is very low and that SO<sub>4</sub><sup>2-</sup> is not a limiting factor regardless of the high SRR.

#### *The desiccation horizon*

The desiccation horizon of the early 19th century drought, which is prominent in all affected lake sediments (Nicholson, 1998; Verschuren, 1999a; Bessems et al., 2008; De Cort et al., 2013), was located in a depth of 60 cm to 80 cm. The horizon formed when the respective lakes fell dry and it is a stiff layer consisting of older, oxidised, and compacted lake sediments (Verschuren et al., 1999b).

In the desiccation horizon, increased amounts of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> and lower amounts of NH<sub>4</sub><sup>+</sup> were detected (fig. 3.10). The nitrification process, which converts NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup> and finally NO<sub>3</sub><sup>-</sup>, requires oxygen, which is not present in the desiccation horizon since oxygen penetration is only a few millimetres into the sediment. Experiments have shown that NH<sub>4</sub><sup>+</sup> can be oxidised under anoxic conditions and in the presence of iron to NO<sub>2</sub><sup>-</sup> and that simultaneously ferrous iron (Fe<sup>3+</sup>) is reduced to ferric iron (Fe<sup>2+</sup>; Clément et al., 2005). In those experiments, NO<sub>2</sub><sup>-</sup> was enriched, but no NO<sub>3</sub><sup>-</sup> was produced. The latter is produced under anoxic conditions when NH<sub>4</sub><sup>+</sup> is oxidised with manganese oxides (Luther III and Popp, 2002). Since the sediment of Lake Oloiden is richer in iron than manganese (Tarras-Walshberg, 1986; the sediments of Lakes Naivasha and Oloiden are similar), the higher amounts of NO<sub>2</sub><sup>-</sup> compared to NO<sub>3</sub><sup>-</sup> fit. Additionally, NO<sub>3</sub><sup>-</sup> is also used to reoxidise the Fe<sup>2+</sup> to Fe<sup>3+</sup>, additionally increasing the amount of NO<sub>2</sub><sup>-</sup>.

The elevated amounts of SO<sub>4</sub><sup>2-</sup> in the desiccation horizon can be explained in a similar way: It has been shown that sulphate reducers and related organisms are capable of oxidising ES to SO<sub>4</sub><sup>2-</sup> if manganese is present as an electron acceptor (Lovley and Phillips, 1994). It is safe to



assume that ES is present in the desiccation horizon of Lake Oloiden, because it was deposited in large amounts in all sediment cores analysed for reduced sulphur species (TRIS) during times of low lake levels (see subchapters 3.2.B, 3.3.B, 3.5.B, 3.8.B).

The question, why those redox reactions just take place within the desiccation horizon, may be explained by the fact that the sediment was oxidised when the lake fell dry. Sedimentary iron and manganese were oxidised and could be used for  $\text{NH}_4^+$  oxidation. The sediment above the horizon is reducing and therefore no adequate reagents for the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  or  $\text{NO}_3^-$  are present.

The prominent negative excursions of  $\text{Br}^-$  and  $\text{PO}_4^{3-}$  may be tied to the  $\text{NH}_4^+$  oxidation, because those excursions were not seen in the desiccation horizon of Lake Sonachi, although conditions are expected to be similar (see subchapter 3.8.B). Of course, other reasons for those excursions cannot be ruled out.

Most of the biomarkers in Lake Oloiden did not show large variations throughout the sediment core. In the sample directly above the desiccation horizon only few biomarkers were present, mainly long-chain *n*-alkanes and hopenes. Verschuren et al. (1999b) reported that the lake level was shallow with large seasonal fluctuations after the drought ended. It is possible that organic-matter input into this lake was very low and that this is the reason why only few biomarkers were detected in the depth interval directly above the desiccation horizon.

#### *Influence of Lake Naivasha*

Some biomarkers in the sediment core of Lake Oloiden showed similar exponential increases as the respective biomarkers in Lake Naivasha, e.g. long-chain compounds, saturated short-chain *n*-fatty acids, benzofuranones, and carotenoids (fig.3.11). If those biomarkers were related to the floriculture around Lake Naivasha, than the year 1980 would be located approximately in 20 cm b.l.f., which would imply similar sedimentation rates for both lakes. The year 1980 marks the approximate start of floriculture in the vicinity of Lakes Naivasha and Oloiden; but just two years later the two lakes got separated. Consequently, the biomarker increases can either be related to floriculture or to the distinctness of Lake Oloiden. When the latter got separated from Lake Naivasha, its salinity increased and the planktonic community changed to more salt-tolerant species (e.g. cyanobacteria). Consequently, benzofuranones and carotenoids, which originate from cyanobacteria, increased due to the increasing salinity of the lake. The long-chain compounds, on the other hand, might be more related to floriculture, because they are usually of terrestrial origin. Because no rivers flow directly into Lake Oloiden, an exponential increase of terrestrial input unrelated to floriculture is less likely.

### *Salvinia outbreak*

A fluid and rotten smelling layer between 10 cm and 20 cm is another interesting aspect in the sediment core of Lake Oloiden. Only in that layer, large concentrations of phytosterols, phytol, and two isoalkanes were detected. Additionally, the *n*-C<sub>27</sub> alkane was more dominant in the *n*-alkane distribution in that depth interval. All those biomarkers might be connected to a large outbreak of the freshwater fern *Salvinia molesta* in the early 1980s when Lake Oloiden was still confluent with Lake Naivasha (Verschuren et al., 1999b). That particular layer was not detected in the sediment column of Lake Naivasha which can be either explained by an overprint due to floriculture or because *Salvinia* did not spread to the coring site.

## **3.8. Lake Sonachi**

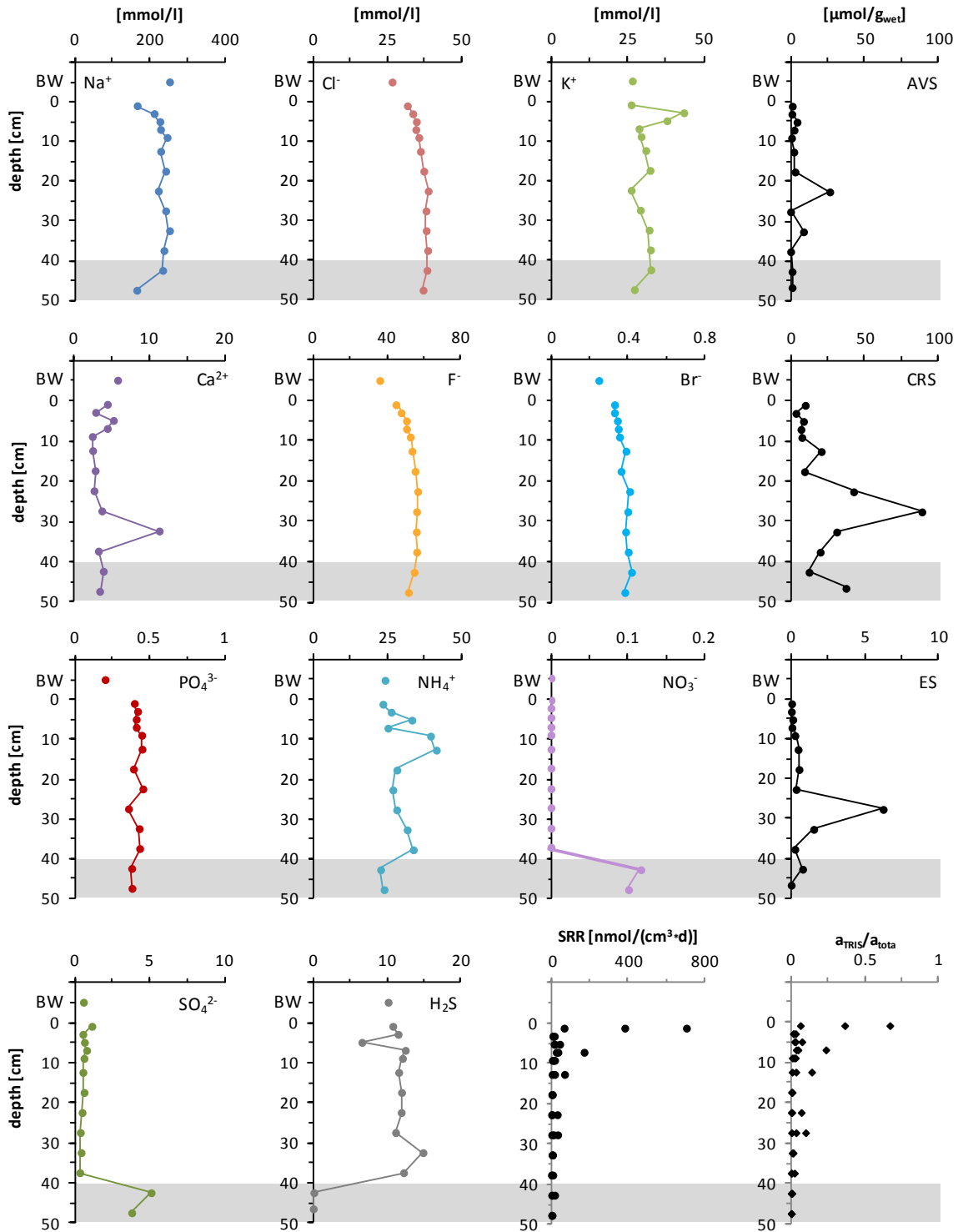
### **3.8.A. Results**

#### *Lake and porewater chemistry*

In Lake Sonachi, bottom and surface water showed strong differences regarding conductivity and salinity. Conductivity and salinity in the surface water were 12 000 µS/cm and 12 g/l, respectively; in the bottom water, the values were significantly higher with 28 000 µS/cm for conductivity and 23 g/l for salinity. The pH values of bottom and surface water were similar with roughly 10.0.

Dissolved ions found in the sediment porewater of Lake Sonachi included Na<sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, F<sup>-</sup>, Br<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> (see depth profiles in fig. 3.12). H<sub>2</sub>S was also found. In general, the distribution patterns of the single ions were stable throughout the core. K<sup>+</sup> and Ca<sup>2+</sup> distributions showed both a distinct peak in the upper part of the core (3 cm to 5 cm); additionally, a second peak was found in 32.5 cm of the Ca<sup>2+</sup> depth profile. NH<sub>4</sub><sup>+</sup> showed more variations with lower concentrations in the desiccation horizon. SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>S concentrations above the desiccation horizon were stable and NO<sub>3</sub><sup>-</sup> was not detected in the 'normal' sediment. In the desiccation horizon, however, SO<sub>4</sub><sup>2-</sup> concentrations increased significantly and H<sub>2</sub>S was not detectable. NO<sub>3</sub><sup>-</sup> was also found in the desiccation horizon.

In order to calculate the relative abundances of the ions in the porewater of Lake Sonachi, the average concentrations of the single anions and cations of the whole core were taken. The most abundant ions were F<sup>-</sup> and Na<sup>+</sup> representing 57.0 % of the anions and 76.6 % of the cations, respectively. Other important constituents were Cl<sup>-</sup> (39.2 % of anions), K<sup>+</sup> (10.6 % of cations), and NH<sub>4</sub><sup>+</sup> (9.9 % of cations). Minor components were Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> with 2.8 % or less.



**Fig. 3.12:** Results of the porewater analysis and reduced sulphur species as well as sulphate reduction rates of Lake Sonachi. The grey layer located below 40 cm b.l.f. shows the position of the desiccation horizon of the early 19th century drought. BW: bottom water. For  $\text{Ca}^{2+}$  see subchapter 4.1.A.

### *Reduced sulphur species and sulphate reduction rates*

In the sediment core of Lake Sonachi, all three reduced sulphur fractions were detected in low concentrations (see fig. 3.12). Significantly higher values were detected in 22.5 cm for AVS and 27.5 cm for CRS and ES.

Sulphate reduction rates in the sediment core of Lake Sonachi showed strong variations in the uppermost sample, varying between 66 nmol/(cm<sup>3</sup> × d) and 710 nmol/(cm<sup>3</sup> × d). The values decreased to 4.6 nmol/(cm<sup>3</sup> × d) in 32.5 cm b.l.f. and remained constant throughout the rest of the sediment core.

The ratio  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  decreased from 0.67 at the top to 0.01 in 32.5 cm and stayed constant below that depth.

### *Organic geochemistry*

The important biomarkers found in Lake Sonachi are listed in table 3.5 and the respective diagrams are shown in figure 3.13.

The total biomarker concentration in the sediment core of Lake Sonachi decreased from values of 1 279 µg/g<sub>dry wt.</sub> at the surface to 886 µg/g<sub>dry wt.</sub> in the desiccation horizon in 40 cm to 52 cm b.l.f. with two distinct maxima in 9 cm and 22.5 cm. The trends of the single biomarker concentrations were highly variable, although a decreasing trend with depth was evident for most biomarkers. Except long-chain *n*-alkanols, all biomarkers were below the detection limit within the desiccation horizon.

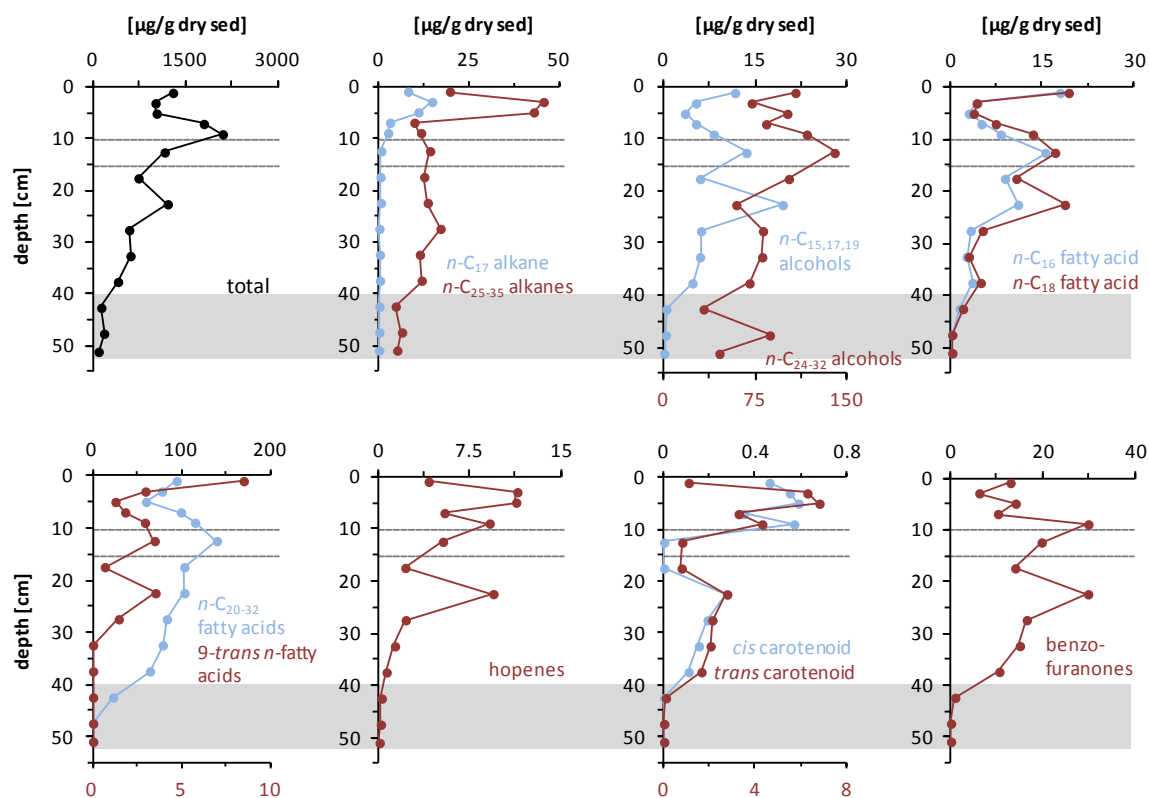
## **3.8.B. Key characteristics**

### *Sulphate reduction*

In the uppermost sample, SRR and  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  showed large variations. The high  $a_{\text{TRIS}}/a_{\text{TOTAL}}$  ratios of up to 0.7 show that the turnover of SO<sub>4</sub><sup>2-</sup> is high and that calculated SRR are not reliable. In contrast to Lake Oloiden, SRR do not increase in the desiccation horizon. Sulphate cannot be the limiting factor, because SO<sub>4</sub><sup>2-</sup> concentrations even exceed concentrations of the desiccation horizon of Lake Oloiden.

### *Desiccation horizon*

Like in Lake Oloiden, a desiccation horizon was located at the core bottom of Lake Sonachi, corresponding to the early 19th century drought (Verschuren et al., 1999a). Interestingly, no NO<sub>2</sub><sup>-</sup> was detected in the horizon and Br<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> concentrations stayed constant (fig. 3.12), which contrasted with the observations made in Lake Oloiden (see fig. 3.10). The absence of



**Fig. 3.13:** Results of the biomarker analysis of Lake Sonachi. The grey layer located below 60 cm b.l.f. shows the position of the desiccation horizon of the early 19th century drought.

**Table 3.5:** The table shows the important biomarkers found in Lake Sonachi. n.a. = not attributed.

group	biomarker	origin
<i>n</i> -alkanes	<i>n</i> -C <sub>17</sub> <i>n</i> -C <sub>25</sub> – <i>n</i> -C <sub>35</sub> ( <i>long-chain n-alkanes</i> )	algae higher plants
<i>n</i> -alkanols	<i>n</i> -C <sub>15</sub> ; <i>n</i> -C <sub>17</sub> ; <i>n</i> -C <sub>19</sub> ( <i>short-chain n-alkanols</i> ) <i>n</i> -C <sub>24</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-alkanols</i> )	n.a. higher plants
saturated <i>n</i> -fatty acids	<i>n</i> -C <sub>16</sub> & <i>n</i> -C <sub>18</sub> ( <i>short-chain n-fatty acids</i> ) <i>n</i> -C <sub>20</sub> – <i>n</i> -C <sub>32</sub> ( <i>long-chain n-fatty acids</i> )	various higher plants
unsaturated <i>n</i> -fatty acids	9- <i>trans n</i> -C <sub>13</sub> , <i>n</i> -C <sub>15</sub> , <i>n</i> -C <sub>16</sub> , <i>n</i> -C <sub>18</sub>	bacteria
hopenes	hop-22(29)-ene I, II & III; hop-17(21)-ene; hop-21(22)-ene I & II	bacteria
carotenoids	4,5-didehydro-5,6,7,7',8,8',9,9',10,10',11,11',12,12',13,13', 14,14'-octadecahydro-β,β-carotene ( <i>cis</i> & <i>trans</i> isomers)	cyanobacteria
benzofuranones	6-hydroxy-4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1-benzofuran-2(4H)-one ( <i>loliolide</i> ) 4,4,7α-trimethyl-5,6,7,7α-tetrahydro-1-benzofuran-2(4H)-one ( <i>dihydroactinidiolide</i> )	xanthophylls carotenes

iron might explain the absence of  $\text{NO}_2^-$  since the anaerobic oxidation of  $\text{NH}_4^+$  needs oxidised iron. Another explanation is the absence of bacteria which use iron to oxidise  $\text{NH}_4^+$ .

The very low organic matter concentration in the desiccation horizon was explained by Verschuren et al. (1999a) by the advanced mineralisation of organic matter during the desiccation period. The biomarkers in this study seem also to be affected by that mineralisation, because except long-chain *n*-alkanes and *n*-alkanols no biomarkers were present in significant amounts (fig. 3.13).

#### *Anoxygenic photosynthetic activity*

Due to the two distinct peaks in the total biomarker concentration, the desiccation horizon, and the layer of colloidal silica (see fig. 3.12), it was possible to correlate the sediment core of Lake Sonachi with the depth-age profile of Verschuren (1999b). According to that study, the water level of Lake Sonachi fell about 6 m in the early 20th century and stayed low until 1930 (approximately in 20 cm to 30 cm b.l.f. in this study's sediment core). That drop in lake level did not interrupt the meromictic mixing regime of the lake (Verschuren, 1999b), but it might have allowed light to penetrate to the sediment surface. If that was the case, then anoxygenic photosynthetic activity would have been possible and CRS and ES could have been deposited in the sediment (see also subchapter 3.5.B). A further decline in lake level led to, at least partially, oxygenated conditions at the lake bottom so that anoxygenic photosynthesis and consequently the deposition of CRS and ES ceased.

#### *Colloidal silica*

In the sediment core of Lake Sonachi, colloidal silica was found in the sediment layer between 10 cm to 15 cm, which was already reported by Kilham and Hecky (1973) as well as Verschuren (1999b). Verschuren (1999b) suggested diatom frustules as the source of those silica layers, since the concentration of a diatom-characteristic pigment was quite high in that depth. It has been proposed that the colloidal silica precipitated abiogenically when large amounts of freshwater decreased the pH of silica-saturated, high pH lake water to values lower than 9 (reference in Verschuren, 1999b). Those silica layers represent the precursors of bedded cherts found in ancient, alkaline and saline playa deposits (references in Verschuren, 1999b). In the sediment core of Lake Sonachi, biomarkers, which were rare throughout the rest of the core, were found in large amounts in that layer (i.e. methyl-3-hydroxycholest-5-en-26-oate, 2-methylnonadecane, 1,13- $\text{C}_{30}$  and 1,15- $\text{C}_{32}$  diols, nonadec-14-ene) and are obviously related to silica precipitation. No carotenoids were detected in the silica layer, which strongly points to a decline in cyanobacteria due to the freshwater input.

The background features three large, solid green circles of varying sizes. One is in the top right, one is in the middle right, and one is in the bottom right. Two thin green lines cross the page diagonally, one from the top left to the middle right, and another from the top right to the bottom right.

## **Chapter 4:**

# **Comparison of the lake sediments**





## 4.1. General comparison of the lakes

### 4.1.A. Water characteristics and sulphate reduction

#### *Lake properties*

The seven studied lakes varied significantly in their lake water properties (table 4.1). Regarding conductivity, salinity, and pH, the lakes can be divided into three groups: One group (group I in table 4.1) consists of the two freshwater Lakes Baringo and Naivasha, which were characterised by low salinities, low conductivities, and moderate pH values (around 8). Both lakes can maintain their freshwater character because they have large drainage areas and likely possess subsurface outflows (Dunkley et al., 1993; Stoof-Leichsenring et al., 2011). A second group (group III in table 4.1) consists of the hydrologically closed Lakes Logipi, Eight, and Bogoria, which were characterised by high conductivities/salinities ( $> 41\,000\ \mu\text{S}/\text{cm}$ ;  $> 31\ \text{g}/\text{l}$ ) and pH values (around 10). All three lakes are classified as hypersaline (Foti et al., 2007) and are located in the northern part of the Kenyan Rift Valley, where evaporation exceeds  $4\,000\ \text{mm}/\text{a}$  (Dunkley et al., 1993; Junginger, 2011) and precipitation is lower than  $650\ \text{mm}/\text{a}$  (Castanier et al., 1993; [www.climatedata.eu](http://www.climatedata.eu)). Lake Bogoria showed a pronounced density stratification due to its relative steepness and its position in a trough (Harper et al., 2003). The remaining two lakes (group II in table 4.1) Lakes Oloiden and Sonachi had equally high pH values (around 10) as group III, but salinities were lower, varying between  $5\ \text{g}/\text{l}$  and  $23\ \text{g}/\text{l}$ . Those salinities are characteristic for hyposaline lakes (Foti et al., 2007). Lakes Oloiden and Sonachi are satellite lakes of Lake Naivasha and both are influenced by the latter via groundwater flow (Verschuren, 1999a) and therefore are less saline than the lakes of group III. Additionally, the salinity of Lake Oloiden is reduced when the lake reunites with Lake Naivasha during high stands. Lake Sonachi showed, like Lake Bogoria, a pronounced density stratification which is only present in the morning (when the cores for this study were taken) and which breaks up in the afternoon (Verschuren et al., 1999).

Temperature and evapotranspiration have a strong influence on the salinity of an endorheic lake. The higher those parameters are the higher is the salinity of the lake. It can be seen that salinity and conductivity of the saline lakes increase in south-northern direction as do temperature and evapotranspiration. A similar trend is obvious for the two freshwater lakes. No gradient was observed for the pH values.

**Table 4.1:** Table showing the conductivity, salinity, and pH of the bottom and surface water of the studied lakes.

group	Lake	surface water			bottom water		
		conductivity [ $\mu\text{S}/\text{cm}$ ]	salinity [g/l]	pH	conductivity [ $\mu\text{S}/\text{cm}$ ]	salinity [g/l]	pH
I	Baringo	450	-	8.0	-	-	-
	Naivasha	219	2	8.4	245	2.5	7.9
II	Oloiden	6 300	7	9.8	6 200	5	9.8
	Sonachi	12 000	10	10.0	28 000	23	9.9
III	Logipi	42 300	31	9.7	46 000	32	9.8
	Eight	54 300	44	9.9	56 300	50	9.6
	Bogoria	41 000	40	10.0	61 000	70	9.8

#### *Explanation for high calcium concentrations*

Calcium is an important compound in mafic environments like the Kenyan Rift Valley (Logatchev et al., 1972; Castanier et al., 1993). Although some lakes and inflowing rivers have been reported to be saturated with regard to calcite (Castanier et al., 1993; Verschuren, 2001, Tarits et al., 2006), other articles reported very low concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in Kenyan lake waters (e.g. Gaudet and Melack, 1981; Dunkley et al., 1993; Gaciri and Davies, 1993). This was always explained by precipitation of both cations as carbonates within the catchment of the lakes due to the hot and dry climate in the region.

It is important to notice that most of the relevant articles did not mention acidifying the samples after taking them (e.g. Kilham and Hecky, 1973; Castanier et al., 1993; Renaut et al., 2002; Tarras-Wahlberg et al., 2002; Oduor et al., 2003), which is essential to prevent carbonate precipitation. Additionally, the atomic absorption spectroscopy (AAS) used in the majority of those studies is problematic for  $\text{Ca}^{2+}$  determinations, because of interferences by other substances like ascorbic acid. In one other study (Gizaw, 1996), the samples were acidified and analysed using ICP-AES, a similar reliable tool for  $\text{Ca}^{2+}$  measurements as the ion chromatography employed in this study. But also in this study, no  $\text{Ca}^{2+}$  was detected. The possibility that the detected cation in this study was not  $\text{Ca}^{2+}$  can be excluded, since the samples foamed when HCl was added, proving that  $\text{Ca}^{2+}$  is definitely present in the water.

Calcium concentrations in the sediment columns are likely influenced by mineral formations and conversions, since the concentrations did not follow the general trends of the other ion concentrations.

#### *Unknown cation*

The unknown cation eluting directly before  $\text{Ca}^{2+}$  in all saline lakes might either be cobalt or zinc which both elute before  $\text{Ca}^{2+}$  (M. Lappé, personal communication). Cobalt and zinc have been reported, for example, in Lakes Logipi (Castanier et al., 1993; zinc only), Baringo (Tarits et al., 2006), and Naivasha (Tarras-Wahlberg et al., 2002), although cobalt concentrations were in all cases very low. The concentrations were in fact so low, that they probably would be under the detection limit for ion chromatography. Therefore, it is much more likely that zinc is the unknown cation.

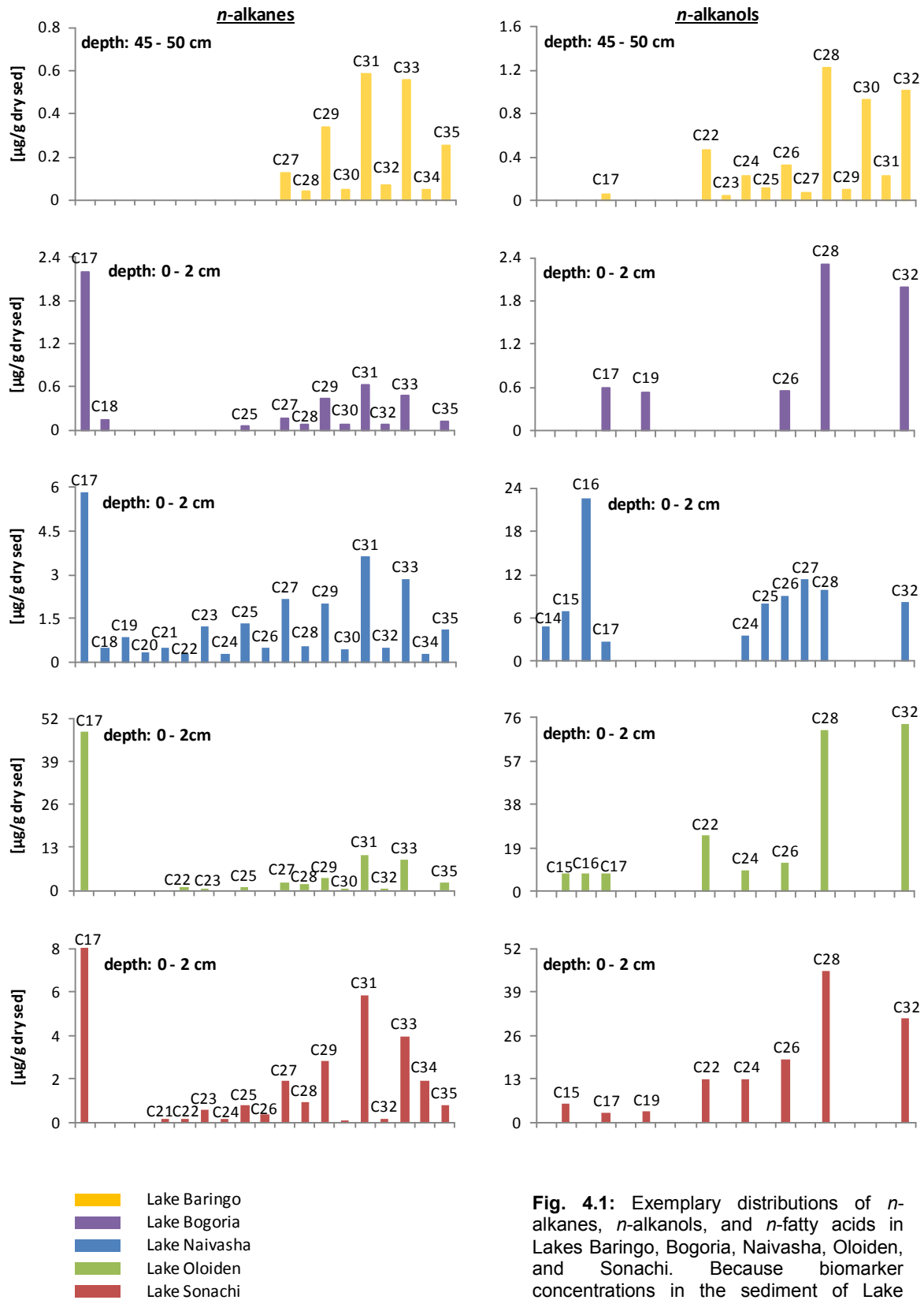
#### *Sulphate reduction rates*

Although sulphate reduction rates varied significantly between  $1.36 \text{ nmol}/(\text{cm}^3 \times \text{d})$  in Lake Baringo and  $710 \text{ nmol}/(\text{cm}^3 \times \text{d})$  in Lake Sonachi, a lot of those values were not accurate, because the turnover of  $\text{SO}_4^{2-}$  was too high (see fig. 3.4, 3.6, 3.8, 3.10 und 3.12). If this is the case then reduced sulphur compounds can be reoxidised to  $\text{SO}_4^{2-}$  which distorts calculated sulphate reduction rates (SRR). Maximum turnover rates of 10 % are considered to lead to accurate results. In the sediment of Lake Naivasha, for example, the turnover of  $\text{SO}_4^{2-}$  was almost 100 % throughout the whole core, whereas it was only 0.4 % in the sediment of Lake Bogoria. These values indicate that the calculated SRR in Lake Bogoria were accurate, whereas in Lake Naivasha they were not. In Lakes Oloiden and Sonachi, calculated SRR were only accurate below 10 cm of the respective cores, but not above that depth. In order to get accurate values for the affected samples, incubations have to be repeated with either higher amounts of  $\text{SO}_4^{2-}$  tracer or with shorter incubation times.

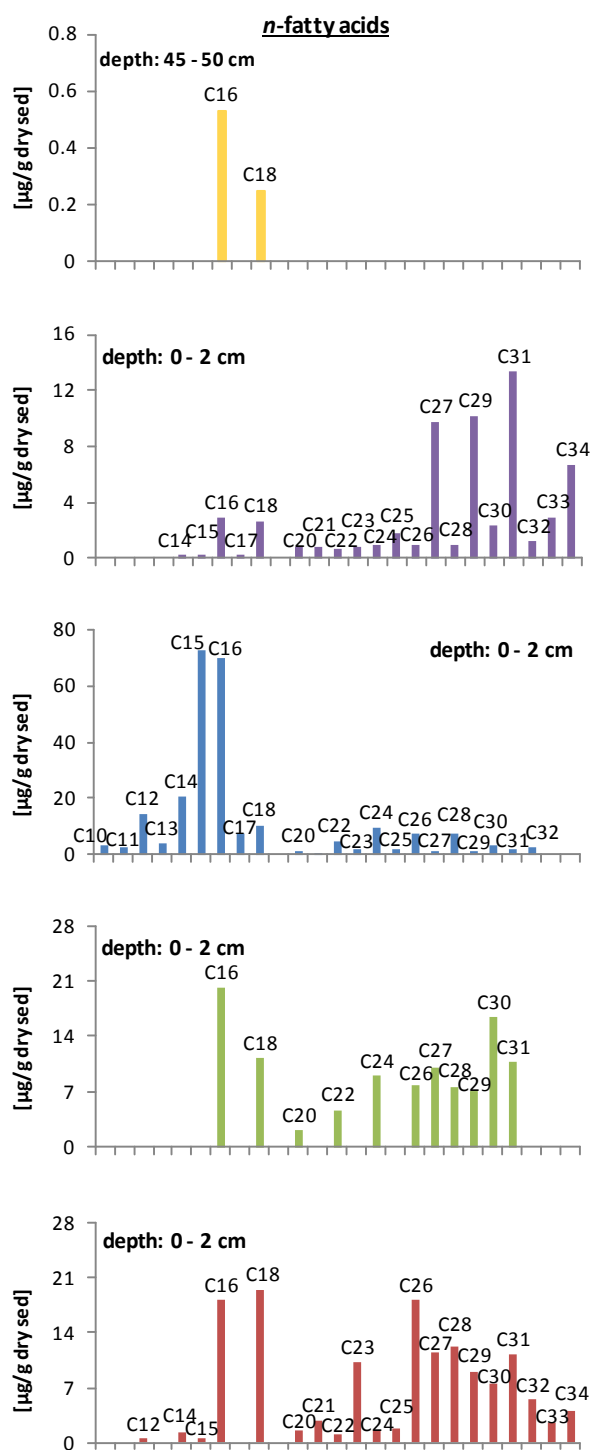
### **4.1.B. Organic geochemistry**

#### *Total biomarker concentration*

The total biomarker concentration, which includes all detected substances, varies significantly between the single lakes (see fig. 3.5, 3.7, 3.9, 3.11, 3.13). The area around Lakes Naivasha and Oloiden is densely populated and intensively used for agriculture (mainly cut flowers), which leads to an increase in the input of biomarkers associated with this kind of human activity. Human activity around Lake Bogoria, on the other hand, is very low, which explains why the total biomarker concentration was much lower in this lake. The organic matter in Lake Baringo is diluted by the high sediment input into that lake, decreasing the biomarker concentration per depth interval.



**Fig. 4.1:** Exemplary distributions of *n*-alkanes, *n*-alkanols, and *n*-fatty acids in Lakes Baringo, Bogoria, Naivasha, Oloiden, and Sonachi. Because biomarker concentrations in the sediment of Lake Baringo were very low, a different depth interval was chosen.



#### Distribution of straight-chain compounds

The distributions of *n*-alkanes, *n*-alkanols, and *n*-fatty acids generally showed bimodal distribution patterns in all five lakes (fig. 4.1). In all cases, long-chain compounds ranging roughly between *n*-C<sub>23</sub> and *n*-C<sub>35</sub> and one or two short-chain compounds dominated. Such distributions are usually found in lake sediments, because they are usually influenced by terrestrial and algal inputs.

The strong predominance of odd-numbered *n*-alkanes and even-numbered *n*-alkanols and *n*-fatty acids are characteristic for biosynthesised compounds and undegraded sediments (e.g. Eglinton and Hamilton, 1967; Kvenvolden, 1967; Cranwell, 1974; Nishimura and Baker, 1986; Grimalt et al., 1991). The only exceptions were the sediments of Lakes Oloiden and Sonachi where the amounts of odd- and even-numbered *n*-fatty acids were equally high (see next paragraph). The predominance of odd-numbered *n*-alkanes and even-numbered *n*-alkanols and *n*-fatty acids, respectively, was still evident in deeper parts of the sediment cores.

The distributions of *n*-alkanols in the single lakes were often incomplete; especially odd-numbered homologues were often missing. The concentrations of those *n*-alkanols must have been under the detection limit, because a co-elution with other compounds can safely be excluded. Especially the absence of the *n*-C<sub>30</sub> homologue was strange, because it was often the only even-numbered long-chain *n*-alkanol missing.

Short-chain compounds had their highest abundances in the upper parts of the cores and then decreased, because they are less stable than the long-chain homologues. That observation was not true for Lakes Bogoria and Sonachi, where short-chain *n*-alkanols and *n*-fatty acids followed the general pattern of other biomarkers (see fig. 3.7 and 3.13).

Although the distribution patterns of the straight-chain compounds looked similar in all studied lakes, there were some interesting exceptions.

In Lake Bogoria, for example, odd-numbered, long-chain *n*-fatty acids strongly predominated in the uppermost sample. Unfortunately, intensive research did not deliver any indications as to their origin.

In Lake Naivasha, the distribution pattern of long-chain *n*-alkanes ( $\geq n\text{-C}_{23}$ ) pointed to two different sources for those compounds. Long-chain *n*-alkanes have been reported in algae (e.g. Lichtfouse et al., 1994) and therefore the *n*-C<sub>23</sub>, *n*-C<sub>25</sub>, and *n*-C<sub>27</sub> alkanes might originate for some part from submerged and floating macrophytes reported in the lake (e.g. Harped et al., 1995; Tarras-Wahlberg et al., 2002; Otiang'a-Owiti and Oswe, 2007) and observed on the lake surface.

In Lakes Oloiden and Sonachi, the distribution of long-chain *n*-fatty acids was characterised by equal amounts of even- and odd-numbered homologues. In contrast to Lake Sonachi, where both groups stayed dominant throughout the core, the amounts of odd-numbered *n*-fatty acids decreased with depth in Lake Oloiden. Nevertheless, their relative abundances stayed high. Sulphate reduction rates in those lakes were the highest determined in this study and they coincided with the highest amounts of odd-numbered *n*-fatty acids. Those odd-numbered *n*-fatty acids might therefore be associated with a strong microbial reworking.

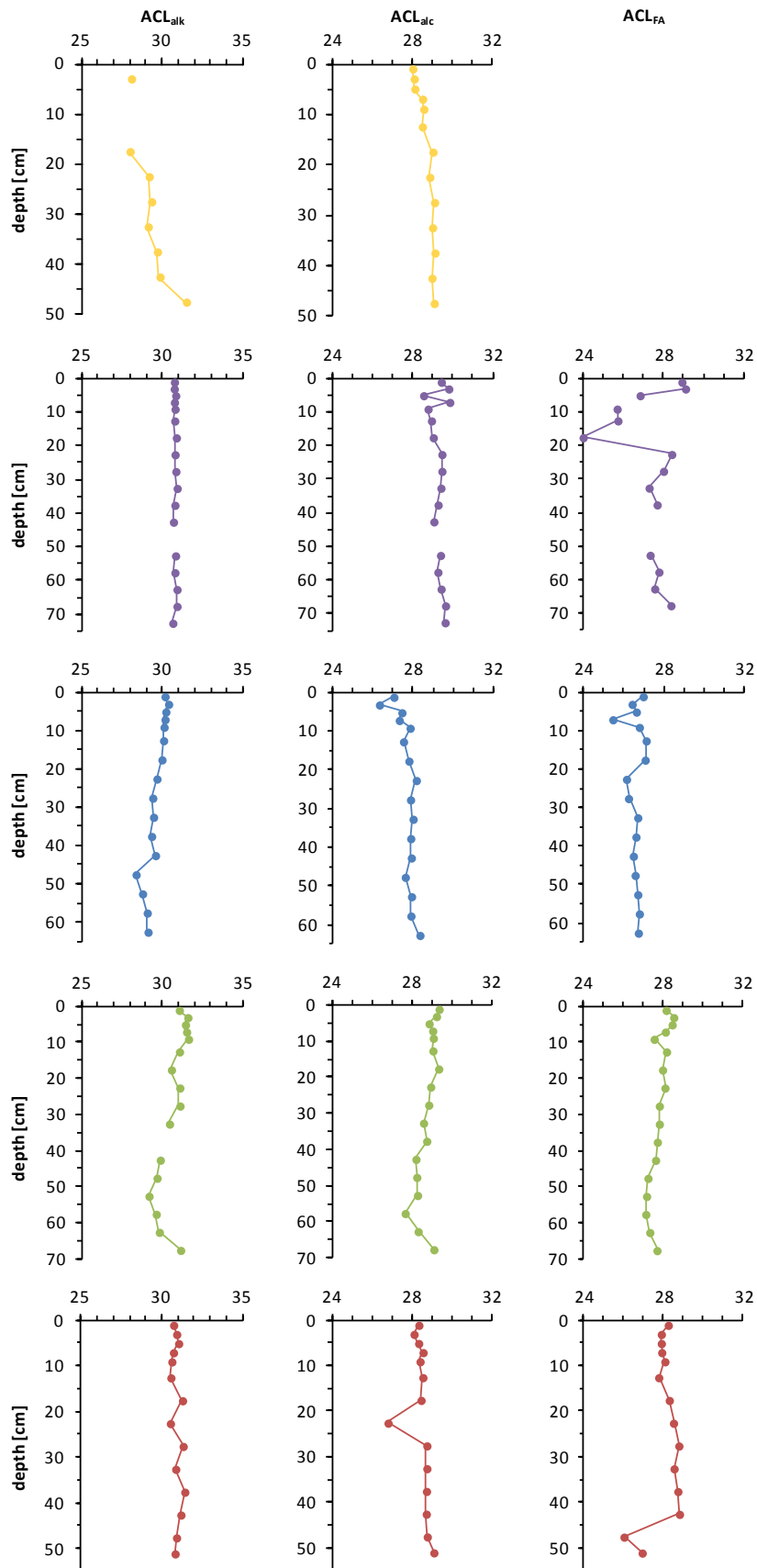
In the three saline Lakes Bogoria, Oloiden, and Sonachi, the odd-numbered *n*-alkanols *n*-C<sub>15</sub>, *n*-C<sub>17</sub>, and *n*-C<sub>19</sub> were the most dominant short-chain *n*-alkanols. Their origin is not known, but they are obviously characteristic for the saline lakes of this study.

#### Average chain length

The average chain length (ACL) describes the average number of carbon atoms based on the abundance of straight-chain compounds (Wang et al., 2014). The ACL of the *n*-alkanes ranging from *n*-C<sub>25</sub> to *n*-C<sub>35</sub> was calculated using the following formula:

$$ACL_{\text{alk}} = \frac{\sum_{k=25}^{35} k \cdot [n\text{-C}_k]}{\sum_{k=25}^{35} [n\text{-C}_k]}$$

[*n*-C<sub>*k*</sub>] was the concentration of the respective *n*-alkane. In a similar manner, the ACLs for the *n*-alkanols (ACL<sub>alc</sub>) and *n*-fatty acids (ACL<sub>FA</sub>) were calculated ranging both from *n*-C<sub>24</sub> to *n*-C<sub>32</sub>.



**Fig. 4.2:** Average chain lengths of *n*-alkanes ( $ACL_{alk}$ ), *n*-alkanols ( $ACL_{alc}$ ), and *n*-fatty acids ( $ACL_{FA}$ ) in Lakes Baringo, Bogoria, Naivasha, Oloiden, and Sonachi. Because no long-chain *n*-fatty acids were detected in the sediment of Lake Baringo, the  $ACL_{FA}$  could not be calculated.

■ Lake Baringo  
■ Lake Bogoria  
■ Lake Naivasha  
■ Lake Oloiden  
■ Lake Sonachi

The  $ACL_{alk}$ ,  $ACL_{alc}$ , and  $ACL_{FA}$  were generally high in all five lakes varying on average between 26.6 and 30.9 in the single sediment columns (fig. 4. 2). In general, no major fluctuations were observed, which usually points to stable inputs of the respective compounds.

It was observed that the  $ACL_{alk}$  was higher ( $> 30.6$ ) in the sediments of the saline lakes than in the sediments of the two freshwater lakes ( $\sim 29.4$ ). A possible explanation for the lower values in the freshwater lakes might be the higher vegetational diversity in the catchment of those lakes. The catchments of the freshwater lakes extend to the rift flanks where the vegetation is different due to higher rainfall and lower temperatures, so that consequently, the diversity of *n*-alkanes might be larger. At least in the case of Lake Naivasha, submerged and floating macrophytes in and on the lake play an important role, because they are probably the origin for the *n*-C<sub>25</sub> and *n*-C<sub>27</sub> homologues. In subchapter 4.3.B it is suggested to use long-chain *n*-alkanes as indicators for hydroclimate.

A similar observation with higher values in the saline lakes was made for the  $ACL_{FA}$ , but not for the  $ACL_{alc}$ .

Nevertheless, the ACLs were not in all cases constant. In Lake Bogoria, the  $ACL_{FA}$  was lower between 20 cm and 5 cm (25.6 instead of 27.8), because long-chain *n*-fatty acids were almost completely missing.

In Lake Naivasha, the  $ACL_{alk}$  slightly increased with the beginning of floriculture from average values of 29.4 to 30.1 which is probably associated with the input of long-chain *n*-alkanes from flowers. Without the influence of floriculture, the  $ACL_{alk}$  would probably have stayed around 29.4. In Lake Oloiden, the same increase of the  $ACL_{alk}$  associated with floriculture was observed, although not as pronounced due to the lower input of plant material. In the lower part of the core of Lake Naivasha (below 45 cm), the  $ACL_{alk}$  was on average lower ( $\sim 28.8$ ). That might actually point to a change in vegetation input. Unfortunately, the age profile only covered the upper 40 cm of this study's core, so that without additional data no assumptions can be made.

In Lake Sonachi, the  $ACL_{alc}$  was constant (28.4) with the exception of a negative excursion in 22.5 cm below the lake floor (b.l.f.) because the *n*-C<sub>30</sub> and *n*-C<sub>32</sub> alkanols were missing. The  $ACL_{FA}$  in Lake Sonachi shows no differences within the sediment core (28.3) excluding the desiccation horizon where it was significantly lower (26.7). The reason for this is the virtually absence of long-chain *n*-fatty acids in this horizon.



#### 4.1.C. Biomarker composition of saline and freshwater lakes

Although the biomarker composition of Lakes Baringo, Bogoria, Naivasha, Oloiden, and Sonachi were similar, there were some interesting and important differences.

There were some biomarkers, which were only found in the saline lakes (e.g. Lakes Bogoria, Oloiden, and Sonachi): the carotenoid isomers, short-chain, odd-numbered *n*-alkanols (*n*-C<sub>15</sub>, *n*-C<sub>17</sub>, and *n*-C<sub>19</sub>), and two sterenes. The carotenoids are probably of cyanobacterial origin, because their precursor,  $\beta$ -carotene, is characteristic for those organisms which are abundant in the saline lakes (Verschuren, 1994; Verschuren et al., 1999; Krienitz et al., 2003; Mavuti and Harper, 2006; Oduor and Schagerl, 2007; De Cort et al., 2013; Schneider, 2013). The origin of the short-chain *n*-alkanols is not known, but their occurrence is restricted to the saline lakes. The specific origin of the two sterenes is also not known, but one of them, stigmasta-3,5-diene, is an intermediate in the degradation of sterols (Killops and Killops, 2013; see also subchapter 4.2.C).

Stigmasterol was the only biomarker which was exclusively found in the two freshwater lakes. This sterol has its origin probably in freshwater algae, where it is often reported (Nishimura and Koyama, 1976; Volkman, 1986; Killops and Killops, 2013).

#### 4.2. Degradation and transformation of organic matter

The degradation of organic matter in microbially active sediments depends largely on the suitability of single compounds as microbial nutrients (Nishimura and Koyama, 1976). The first stages of degradation include hydrogenation, decarboxylation, depolymerisation, and methane fermentation (Nishimura and Koyama, 1976; Killops and Killops, 2013).

Summarised, it can be said that 1) unsaturated compounds are less stable than their saturated counterparts and are therefore readily hydrogenated (Farrington and Quinn, 1971; Nishimura and Koyama, 1976; Killops and Killops, 2013), 2) compounds with functional groups (e.g. *n*-alkanols, *n*-fatty acids) are less stable than compounds missing such groups (e.g. *n*-alkanes; Meyers and Ishiwatari, 1993; Rommerskirchen et al., 2006), and 3) acyclic compounds (e.g. *n*-alkanes) are less stable than cyclic compounds (e.g. hopanoids, steroids; Meyers and Ishiwatari, 1993; Killops and Killops, 2013).

The preservation of organic compounds is improved under anoxic conditions, because the turnover rate of organic matter is lower under anoxic than under oxic conditions (Sun et al., 1997; Killops and Killops, 2013). Additionally, the preservation of unstable compounds is improved if they are closely associated with more resistant compounds (Killops and Killops, 2013).

#### 4.2.A. Degradation of *n*-fatty acids

Biologically produced unsaturated *n*-fatty acids are preferably produced in the *cis* configuration, but in the sediment a clay-catalysed transformation to the *trans* configuration can occur since this isomer is more stable (Van Vleet and Quinn, 1976; Killops and Killops, 2013).

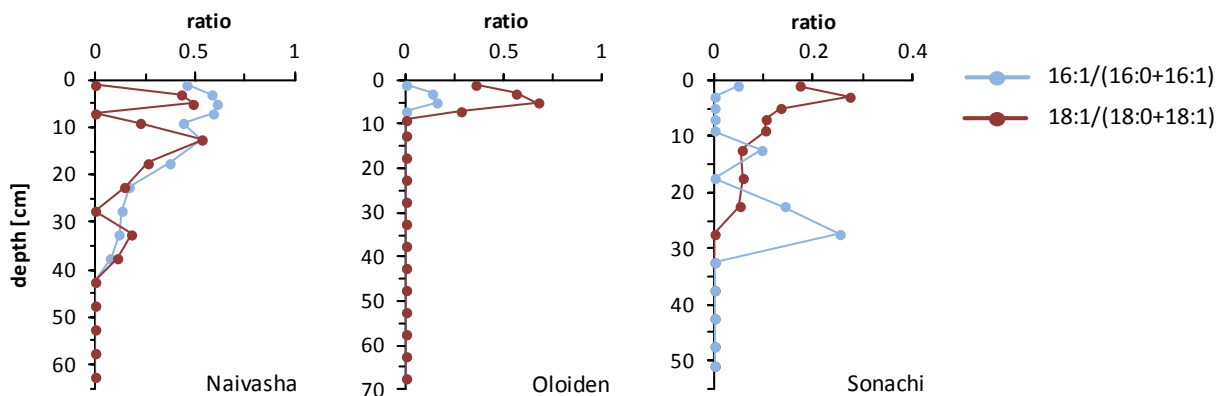
In Lakes Baringo and Bogoria, no unsaturated *n*-fatty acids were detected, either because of a low input into the sediment or a poor preservation in the sediment or water column. In the three southern lakes, only short-chain homologues ranging from *n*-C<sub>13</sub> to *n*-C<sub>18</sub> were detected. In the sediment of Lakes Oloiden and Sonachi, only *trans* homologues were found, which shows that the stability of the *cis* isomers is very low in those sediments. The *trans* isomers disappeared below a depth of 8 cm in Lake Oloiden and 30 cm in Lake Sonachi, respectively, because unsaturated *n*-fatty acids are generally not very stable regarding transformation. In Lake Naivasha, *cis* and *trans* isomers of unsaturated *n*-fatty acids were detected. The *cis* isomers, however, disappeared in lower depths and were present in lower amounts than the respective *trans* isomers which reflects the higher stability of the *trans* isomers. The *cis* isomers were probably only detected in the sediments, because they are produced *in situ*. Unsaturated *n*-fatty acids were almost exclusively detected in the upper 10 cm of the sediment, where a high microbial activity has been assumed.

In the sediment, unsaturated *n*-fatty acids are rapidly converted into their saturated homologues leading to a much faster decrease of unsaturated than saturated *n*-fatty acid concentrations (Kvenvolden, 1967; Farrington and Quinn, 1971; Matsuda, 1978). Polyunsaturated *n*-fatty acids are even less stable than monounsaturated ones (Cranwell, 1974).

In contrast to their unsaturated counterparts, saturated *n*-fatty acids were found throughout all sediment cores. The ratio of unsaturated *n*-fatty acids to their respective saturated homologues shows in all three southern lakes the expected decreasing trend (fig. 4.3). In Lake Oloiden, unsaturated *n*-fatty acids are especially quickly converted, because they were only found in the upper 8 cm of the sediment. The presence of the unsaturated *n*-C<sub>16</sub> fatty acid in only four depth intervals in the sediment of Lake Sonachi is odd, but reflects the poor preservation of unsaturated compounds. A higher input of this *n*-fatty acid might be the reason for its presence in some depth intervals.

It is obvious, that the stability of unsaturated, short-chain *n*-fatty acids is higher in Lakes Naivasha and Sonachi compared to Lake Oloiden.

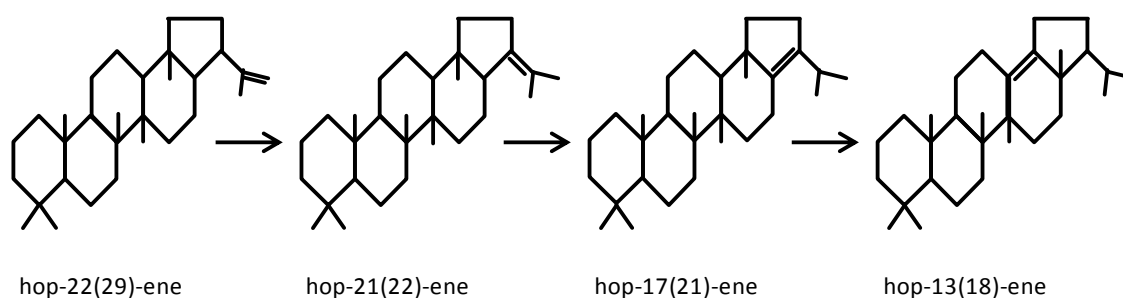
In Lakes Oloiden and Sonachi, the distribution of long-chain *n*-fatty acids was characterised by equal amounts of even- and odd-numbered homologues. It is assumed that those *n*-fatty acids are associated with a strong microbial reworking of organic matter.



**Fig. 4.3:** Ratios of the unsaturated to saturated homologues of  $n$ -C<sub>16</sub> and  $n$ -C<sub>18</sub> fatty acids in Lakes Naivasha, Oloiden, and Sonachi. The terms 16:1 and 18:1 correspond to the unsaturated homologues and 16:0 and 18:0 correspond to the saturated homologues, respectively.

#### 4.2.B. Degradation of hopanoids

Hop-22(29)-ene, also known as diploptene, is a common component of cell membranes in eubacteria, but is also found in ferns (Elvert et al., 2001; Killops and Killops, 2013). When adsorbed onto clays, the double bond may shift to form more stable isomers of hop-22(29)-ene (fig. 4.4). The transformation pathway begins with hop-22(29)-ene which is transformed into hop-21(22)-ene, hop-17(21)-ene, and finally to hop-13(18)-ene (references in Innes et al., 1998; Killops and Killops, 2013). The stability of the single hopene isomers increases along the transformation pathway with hop-13(18)-ene being the most stable one (Killops and Killops, 2013). Although hopenes are generally widespread in recent sediments, hop-17(21)-ene and hop-13(18)-ene are the most abundant (Elvert et al., 2001; Killops and Killops, 2013).



**Fig. 4.4:** Diagenetic pathway of hop-22(29)-ene. Modified after Killops and Killops, 2013

In the sediment cores of the lakes, hop-22(29)-ene, hop-21(22)-ene, and hop-17(21)-ene were detected. Hop-13(18)-ene was not found.

In the three saline Lakes Bogoria, Oloiden, and Sonachi, hop-21(22)-ene was the diagenetically most advanced hopene, whereas in the two freshwater Lakes Naivasha and Baringo hop-

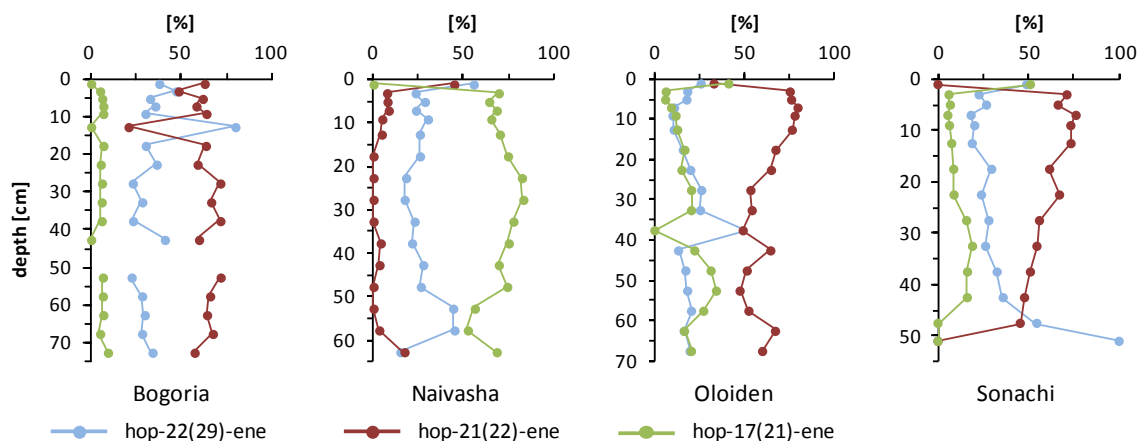
17(21)-ene was the most advanced one (fig. 4.5). It is possible that the high salinity and/or alkalinity in the three saline lakes hinder the transformation of hop-22(29)-ene in the sediment.

In Lakes Bogoria, Naivasha, Oloiden, and Sonachi, the relative amounts of the single hopene isomers were relatively constant. One exception was the sample in 12.5 cm b.l.f. in Lake Bogoria, where the relative amount of hop-22(29)-ene doubled, whereas the relative amounts of the other isomers decreased. The absolute amount of hopenes did not change in that depth. It might be possible that methanogens present in the sediment produce 'fresh' hop-22(29)-ene (Rohmer et al., 1984; Schouten et al., 2001) which is not yet fully converted. In that depth, higher amounts of saturated  $n$ -C<sub>16</sub> and  $n$ -C<sub>18</sub> fatty acids were found which, generally, can be characteristic for microbes (Hatcher et al., 1982; Cardoso et al., 1983).

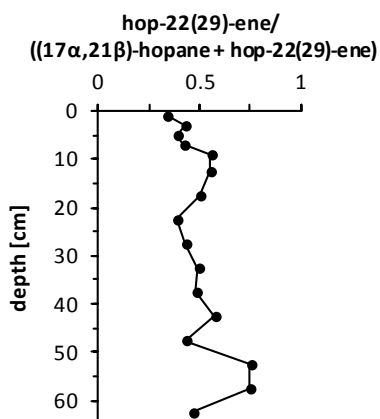
In the desiccation horizon of Lake Sonachi, only hop-22(29)-ene was detected, albeit in low concentrations. However, in the desiccation horizon of Lake Oloiden, all three isomers were detected, although both horizons are similar in their sedimentological composition. But both desiccation horizons differed in their hydrochemical composition (see subchapters 3.7.B and 3.8.B). One possible explanation is that the anaerobic nitrification observed in Lake Oloiden produces hop-22(29)-ene which is then converted to more stable isomers. Since that process was not observed in Lake Sonachi, hopenes are generally not present. Another possibility is that hopenes in Lake Sonachi were quickly recycled when the lake was dry, so that consequently no hopenes were preserved in the horizon.

In Lake Naivasha, just one hop-22(29)-ene isomer was detected. In the saline lakes, however, a second isomer was detected in the sediment, which was also more abundant. Without further information about the exact conformation of those isomers, it remains unclear whether salinity had any influence on the isomer distribution or if it was just a coincidence.

Another transformation pathway of hop-22(29)-ene is saturation to (17 $\alpha$ ,21 $\beta$ )-hopane, although bacteriohopanetetrol may also be the precursor for this hopane (Simoneit, 2005). (17 $\alpha$ ,21 $\beta$ )-Hopane was only found in Lake Naivasha and the ratio of hop-22(29)-ene/(hop-22(29)-ene+



**Fig. 4.5:** Relative amounts of the hopene isomers hop-22(29)-ene, hop-21(22)-ene, and hop-17(21)-ene of Lakes Bogoria, Oloiden, and Sonachi.



**Fig. 4.6:** The ratio of hop-22(29)-ene/((17 $\alpha$ ,21 $\beta$ )-hopane+hop-22(29)-ene) in the sediment core of Lake Naivasha.

(17 $\alpha$ ,21 $\beta$ )-hopane) showed that hop-22(29)-ene cannot be the only precursor for the (17 $\alpha$ ,21 $\beta$ )-hopane since the ratio would then be constantly decreasing (fig. 4.6). Consequently, bacteriohopanetetrol must be an additional source for (17 $\alpha$ ,21 $\beta$ )-hopane.

#### 4.2.C. Degradation of sterols

Saturated sterols ( $\cong$  stanols) are commonly not found in living organisms, although they may be found in diatoms (Nishimura and Koyama, 1976 and references therein), and therefore originate most often from unsaturated sterols ( $\cong$  stenols). Stenols are quickly converted by microorganisms to stanols in young, lacustrine sediments (Gaskell and Eglinton, 1975; Gaskell and Eglinton, 1976; Nishimura and Koyama, 1976; Nishimura, 1982). Consequently, the ratio of stanols to stenols decreases from the sediment surface downwards. The vertical distribution of sterol compounds is additionally influenced by different microbial degradation rates of stenols and stanols (Nishimura and Koyama, 1976). In anoxic sediments sterols can be preserved (Hassett and Lee, 1977; Martins et al., 2007).

The diversity and amount of phytosterols was only in Lake Naivasha high enough for closer inspection. In all other lakes, they must have been either produced in very low amounts or they were rapidly degraded.

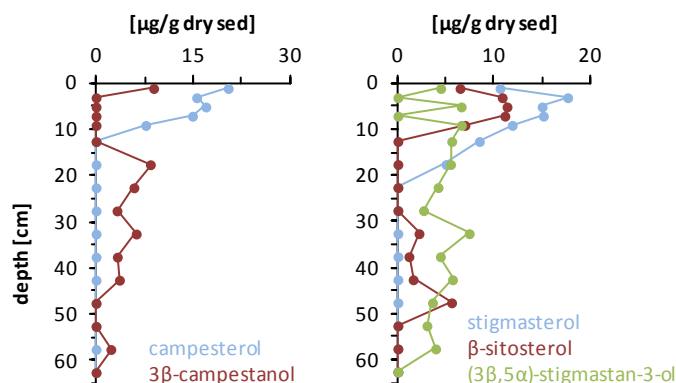
In Lake Naivasha, stenols were mainly present in the upper 25 cm of the sediment core, whereas stanols were mainly present below that depth (see fig. 4.7). That was expected since stenols are rapidly hydrogenated to their saturated counterparts. Stigmasterol, an algal biomarker, increased since the start of floriculture and was probably detected in higher amounts due to a higher algal input. It was not detected in the sediment before that time.

In Lake Oloiden, phytosterols were only found between 10 cm and 20 cm due to an intensive input (see subchapter 3.7.B). Only saturated homologues were found, showing that phytosterols were fast saturated and that they were otherwise not preserved in the sediment.

Cholesterol, a sterol usually associated with algae in aquatic environments, is reduced to  $\beta,\alpha$ -cholestanol in sediments by bacteria (Bethell et al., 1994). In all sediment cores, it was either only detected in the uppermost sample (Lakes Baringo, Oloiden, Sonachi) or not detected at all (Lakes Bogoria, Naivasha). That points to a fast saturation of this molecule. In Lakes Naivasha and Oloiden, the amounts of  $\beta,\alpha$ -cholestanol increased exponentially since the beginning of floriculture. The reason for that are the increasing amounts of algae and consequently the increasing input of cholesterol into the sediment which is rapidly converted to its saturated counterpart. In contrast to Lake Naivasha, cholesterol was and  $\beta,\alpha$ -cholestanol was not detected in the uppermost sample of Lake Oloiden. This shows that the saturation of cholesterol in Lake Oloiden is somewhat slower than in Lake Naivasha. In Lake Sonachi, cholesterol and  $\beta,\alpha$ -cholestanol were both only found in the uppermost sample, which shows, on the one hand, the fast saturation of cholesterol, but also that  $\beta,\alpha$ -cholestanol is not very stable in that environment. It is likely, that this sterol was already converted into a different compound which was not quantified. In Lake Bogoria, the presence of  $\beta,\alpha$ -cholestanol coincides with higher lake levels (see subchapter 3.5.B), so consequently, the produced and deposited amounts must have been significantly higher during those times.

In contrast to the saturation pathway discussed above, cholesterol is reduced to  $\beta,\beta$ -cholestanol inside the gut of mammals, including humans (Brown and Wade, 1984; Martins et al., 2007). During sewage treatment,  $\beta,\beta$ -cholestanol is converted to  $\alpha,\beta$ -cholestanol, so that consequently both sterols can be used to detect faecal pollution (Dutka et al., 1974; Martins et al., 2007). Both isomers are not produced by marine organisms (Brown and Wade, 1984; Martins et al., 2007). In Lake Oloiden, those two isomers were only detected in the two uppermost samples. An anthropogenic input is possible since a village is located directly at the western lake shore. It is possible, that those sterols were already converted into different compounds which were not quantified. Although a large city (Naivasha Town) is located at the eastern shore of Lake Naivasha, neither  $\beta,\beta$ -cholestanol nor  $\alpha,\beta$ -cholestanol was detected. The most likely explanation is that those sterols did not reach the coring site. Inflowing rivers enter the lake from the north and north-east and Naivasha Town is also located on the eastern shore, whereas the coring site is located in the south-western part of the lake. Interestingly,  $\beta,\beta$ - and  $\alpha,\beta$ -cholestanol were found in the upper 15 cm of Lake Bogoria, although this lake is not anthropogenically influenced. It is possible, that those sterols originate from flamingoes which live around the lake in huge numbers.

Instead of saturation, sterols may be further dehydrated to steradienes, which contain an additional double bond (Killops and Killops, 2013). Stigmasta-3,5-diene is such a steradiene and in this study, it was only found in the saline Lakes Bogoria, Oloiden, and Sonachi. In Lake Bogoria, stigmasta-3,5-diene was only found when lake levels were considered to be high and the concentrations were always low (around 60 ppm). It is suggested that the strong density stratification during high lake levels has a significant influence on the preservation of this molecule. This suggestion is further supported by the fact that the preservation of stigmast-3,5-



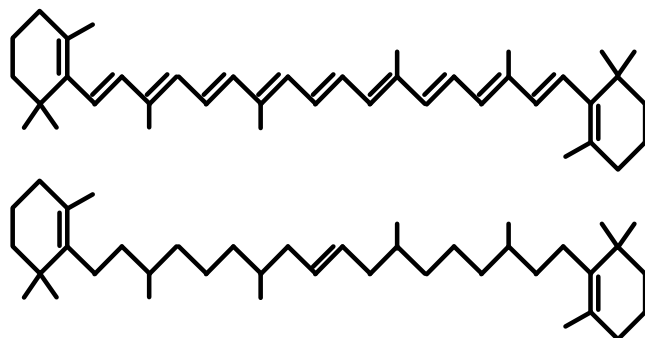
**Fig. 4.7:** Unsaturated and saturated phytosterols in the sediment of Lake Naivasha.

diene in stratified Lake Sonachi is equally good, because it also follows the same general trend. In Lake Oloiden, stigmasta-3,5-diene was mainly found in the upper 20 cm of the sediment column, excluding the uppermost sample. Since the sediment of the lake is virtually devoid of phytosterols (with the exception of the *Salvinia* zone), it is suggested that they are rapidly converted to stigmasta-3,5-diene. This molecule is converted to other molecules below a depth of 20 cm.

#### 4.2.D. Degradation of carotenoids

Carotenoid distributions in sediments are highly influenced by photo-oxidative destruction, herbivore grazing, and bacterial decomposition (Leavitt and Brown, 1988; Leavitt and Carpenter, 1990). They are not very stable regarding degradation even under anoxic conditions, because functional groups are easily removed, rings opened, and chains fragmented (Killops and Killops, 2013). In some cases, however, the complete carotenoid structure can be maintained in a saturated form (Killops and Killops, 2013).

The carotenoid isomers detected in the saline Lakes Bogoria, Oloiden, and Sonachi represent the almost completely saturated form of  $\beta$ -carotene (fig. 4.8). In contrast to this original molecule, these carotenoids had just three double bonds left: one in each of the rings and one in the middle of the chain. The absence of  $\beta$ -carotene in the sediment shows that it is not stable regarding degradation under the present hydrochemical conditions in the lakes.



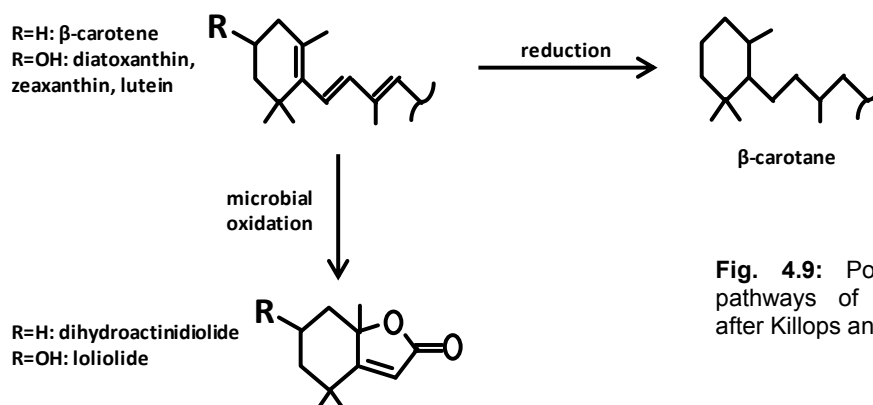
**Fig. 4.8:** The molecule at the top is  $\beta$ -carotene; the one at the bottom is the almost saturated form detected in this study. In the text, it is referred to as the carotenoid, but its IUPAC name is 4,5-didehydro-5,6,7,7',8,8',9,9',10,10',11,11',12,12',13,13',14,14'-octadeca-hydro- $\beta$ , $\beta$ -carotene.

The *cis* and *trans* isomers of the carotenoid show the same trends throughout the three cores, but the *trans* isomer is in all cases about ten times more abundant (see fig. 3.7, 3.11, 3.13). The majority of carotenoids produced by organisms are in the all-*trans* form (Schieber and Carle, 2005; Khoo et al., 2011), which shows that the original isomers of the  $\beta$ -carotene are preserved in the carotenoids. Since the relative abundances of both isomers were not changing with depth, the carotenoids seem to be stable regarding further degradation.

In Lakes Bogoria and Sonachi, the preservation of the carotenoids is especially good due to the permanent anoxic conditions at the lake bottoms. An exception is the silica layer in Lake Sonachi, where carotenoids were almost absent. The huge influx of freshwater necessary to produce those layers might have reduced the cyanobacterial population which represents the main origin for  $\beta$ -carotene. In Lake Oloiden, carotenoids were only present since the separation from Lake Naivasha. Other low-stands were not recorded in the sediment, which suggests that the molecules are converted in a certain depth.

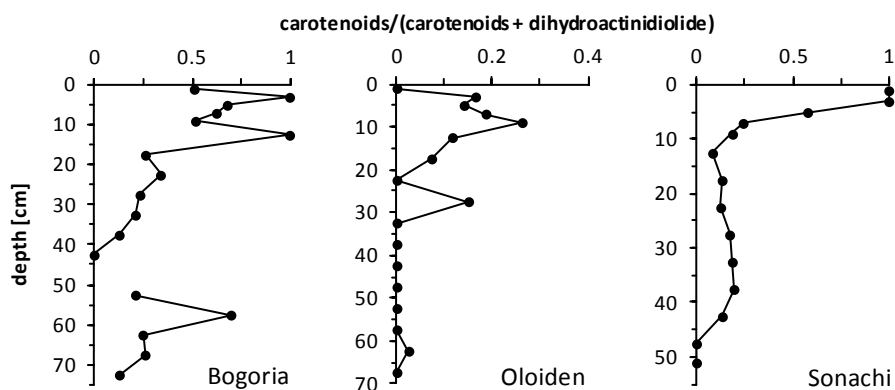
An additional transformation pathway of carotenes is the microbial or photo-oxidation, which eventually results in the formation of dihydroactinidiolide, whereas the equivalent oxidation of xanthophylls yields loliolide (Killops and Killops, 2013; see fig. 4.9). Additional to carotenoids, plants and animals can also be a source for dihydroactinidiolide and loliolide (Isoe et al., 1969; Klok et al., 1984).

The ratio of carotenoids/(carotenoids+dihydroactinidiolide) in Lake Sonachi might actually show the transformation of the carotenoid isomers to dihydroactinidiolide (fig. 4.10). At the top (upper 3 cm) just carotenoids were found. Their relative amounts decreased exponentially to a maximum of 10 % in 12.5 cm b.l.f. This fast transformation of carotenoids is in accordance with a study of Verschuren (1999b) who found that carotenoid degradation in Lake Sonachi is high. The same ratio in Lakes Bogoria and Oloiden did not show this trend, although in Lake Bogoria a general decreasing trend towards the bottom is obvious. Since we did not find the original  $\beta$ -carotene, it is difficult to interpret those diagrams. The two diagenetic pathways of  $\beta$ -carotene, saturation and oxidation, might be more intertwined in Lakes Oloiden and Bogoria than in Lake Sonachi.



**Fig. 4.9:** Possible transformation pathways of  $\beta$ -carotene. Modified after Killops and Killops, 2013





**Fig. 4.10:** The ratio of carotenoids/(dihydroactinidiolide+carotenoids) in the sediment cores of Lakes Bogoria, Oloiden, and Sonachi.

In the freshwater Lake Naivasha, no carotenoid isomers were detected, but the benzofuranones dihydroactinidiolide and loliolide. It is possible that carotenoids are less stable in Lake Naivasha than in the saline lakes and that this is the reason why carotenoids were missing. It is also possible that those benzofuranones have a different origin in Lake Naivasha than in the other lakes, for example diatoms or dinoflagellates (Klok et al., 1984). Dihydroactinidiolide, for instance, was only found until around 1940. From this time on, the area around Lake Naivasha was strongly influenced by human activity and a change in diatom communities (Stoof-Leichsenring et al., 2011). This might indeed indicate an origin from diatoms.

#### 4.2.E. Influence of lake-water chemistry on the degradation of organic material

The salinity, alkalinity, or both seem to have an influence on the transformation of hopenes (see subchapter 4.2.B), which were diagenetically more advanced in the two freshwater Lakes Baringo and Naivasha. The degradation of all other studied biomarkers (i.e. *n*-fatty acids, sterols, carotenoids) was equally far developed in the single lakes independent of their salinity or alkalinity.

In Lakes Bogoria and Sonachi, the stratification of the water column with anoxic bottom water slows the degradation of biomarkers. Consequently, those two lakes are the most useful ones to conduct environmental reconstructions based on biomarkers.

The presence of certain biomarkers (*cis n*-fatty acids, carotenoids, stigmasterol) only in the saline or freshwater lakes, respectively, is related to contrasting inputs rather than differences in preservation.

### 4.3. The lakes as climate archives

#### 4.3.A. Horizons of elemental sulphur as markers for low lake levels?

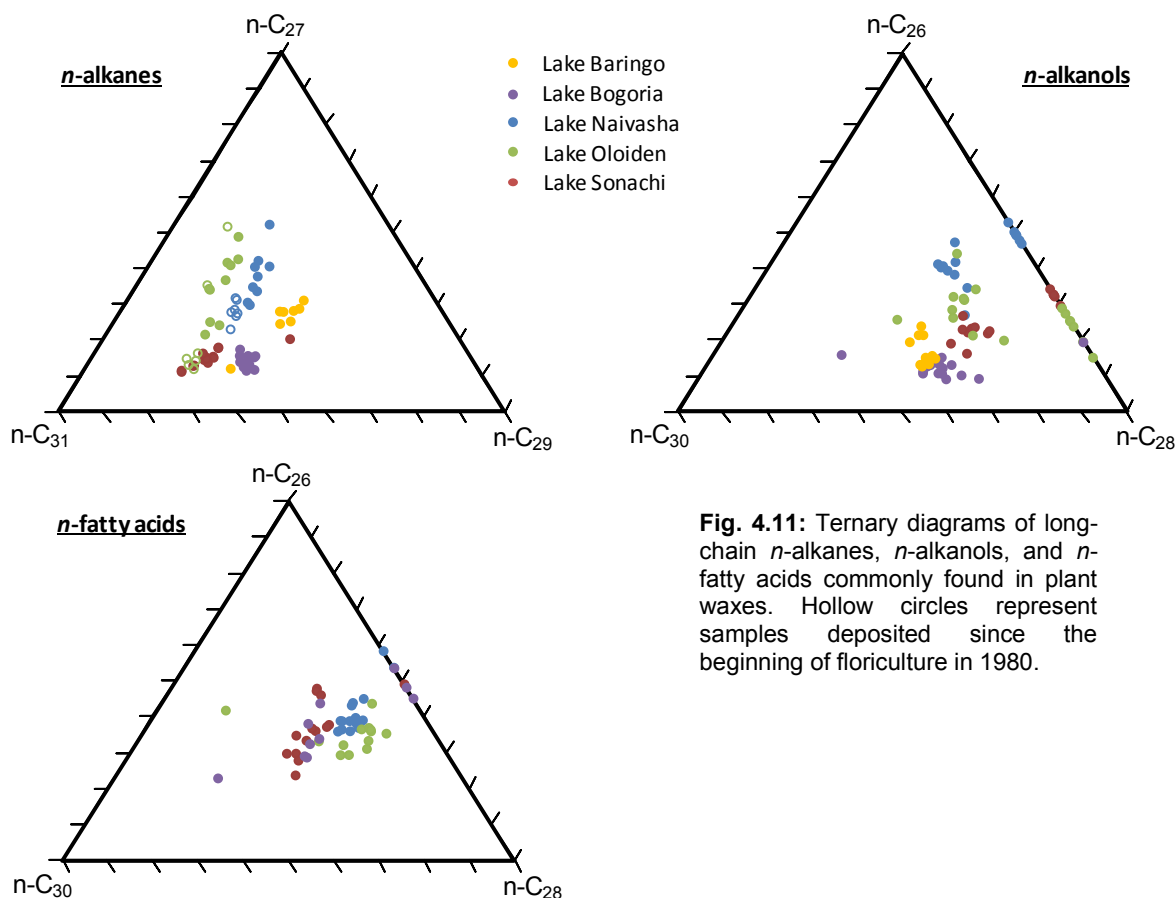
The horizons of elemental sulphur (ES) in Lakes Bogoria and Sonachi were deposited during times when lake levels indeed were lower (see subchapters 3.5.B and 3.8.B). In Lake Eight, the horizon was deposited shortly after the desiccation horizon when lake levels were expected to be low. It is not possible to make assumptions about the lake level of Lake Logipi during the deposition of ES. Nevertheless, it is suggested that those horizons of ES found in Lakes Logipi, Eight, Bogoria, and Sonachi correspond to very low lake levels during the time of deposition. During those low lake levels, oxygen reached the lake bed, allowing sulphide-oxidising bacteria like *Beggiatoa* to grow at the oxic-anoxic interface. When those sulphide-oxidising bacteria died due to increasing lake levels and as a consequence low oxygen levels, they left internally stored sulphur behind. Another possibility is that, during low lake levels, light penetrated deep enough for anoxygenic photosynthesis to occur. This scenario is more likely for Lakes Bogoria and Sonachi since they are generally deeper than Lakes Logipi and Eight. Either way, ES horizons seem to be reliable markers for low lake levels in the past.

#### 4.3.B. Changes in the distributions of straight-chain compounds as indicators for hydroclimate?

Long-chain *n*-alkanes, *n*-alkanols, and *n*-fatty acids are major constituents of higher plants' leaf waxes, where they protect the plant from water loss. It has been observed that some plants produce longer chained compounds when they thrive in a dry and warm environment (e.g. (Schefuß et al., 2003; Hughen et al., 2004; Sachse et al., 2006; Tipple and Pagani, 2013), although not all plant types show this behaviour (Hoffmann et al., 2013). In the study region, the central Lakes Baringo and Bogoria are located in a warmer region ( $\bar{\theta}$  24.6 °C) compared to the southern Lakes Naivasha, Oloiden, and Sonachi ( $\bar{\theta}$  17.2 °C; [www.climatedata.eu](http://www.climatedata.eu)). Precipitation is equally high with roughly 640 mm/a ([www.climatedata.eu](http://www.climatedata.eu)).

The ternary diagrams in figure 4.11 show the relative distributions of *n*-alkanes, *n*-alkanols, and *n*-fatty acids characteristic for land plants.

The ternary diagram of the *n*-alkanes shows that, except two outliers, the *n*-alkanes of Lakes Baringo, Bogoria, and Sonachi cluster, whereas the *n*-alkanes of Lakes Naivasha and Oloiden show more variations. The sediments of Lakes Baringo and Bogoria contain predominantly the longer chain *n*-alkanes *n*-C<sub>29</sub> and *n*-C<sub>31</sub>. Lakes Naivasha and Oloiden, on the other hand, show a higher concentration of *n*-C<sub>27</sub>. This might be attributed to the cooler climate around the southern lakes. If the samples corresponding to floriculture are excluded, then the trend towards the shorter *n*-C<sub>27</sub> homologue is even more evident. The reason for this are probably the flowers



**Fig. 4.11:** Ternary diagrams of long-chain *n*-alkanes, *n*-alkanols, and *n*-fatty acids commonly found in plant waxes. Hollow circles represent samples deposited since the beginning of floriculture in 1980.

grown around the lakes which causes a shift towards longer *n*-alkanes. Lake Sonachi is located in a similar environment regarding temperature and precipitation as Lakes Naivasha and Oloiden, but here the two long-chain homologues dominate; probably because it is a crater lake with its own microclimate and vegetation.

The ternary diagrams of the *n*-alkanols and *n*-fatty acids show that the central lakes have a lower content of the *n*-C<sub>26</sub> alkanol and higher contents of the *n*-C<sub>30</sub> alkanol and *n*-C<sub>30</sub> fatty acid than the three southern lakes. This might again be attributed to the temperature differences in the different parts of the rift. Consequently, long-chain *n*-alkanols and *n*-fatty acids might also represent useful biomarkers to distinguish between regions differing in temperature. The long-chain *n*-fatty acids of Lake Sonachi are again dominated by the long-chain homologue which is probably due to its unique position in a volcanic crater.

Summarised, it can be said that all long-chain compounds can be used to distinguish between the two regions differing in temperature. Due to their strong resistance towards degradation, *n*-alkanes are probably the most reliable ones.

### 4.3.C. Climate versus diagenesis

Regarding the biomarker composition, not all studied lakes are capable of recording climate changes. In Lakes Bogoria and Sonachi, for example, the preservation for the majority of biomarkers is good due to permanently anoxic conditions at the lake bottom. Lake Naivasha, on the other hand, is problematic in this regard, because the biomarker distributions are overprinted by the floriculture present around the lake. The beginning of flower cultivation and its increasing influence on Lake Naivasha are reflected in some biomarker distributions, especially straight-chain compounds, phytosterols, and carboxylate esters. Before the beginning of floriculture, no significant variations in biomarker distributions were detected, making it impossible to say something about climate changes recorded in the sediment. For the other freshwater lake, Lake Baringo, no conclusions concerning its suitability as a climate archive can be drawn due to the high sediment input into the lake and the resulting dilution of biomarkers.

Nevertheless, the lakes possess certain temporal markers beside ES and desiccation horizons. For example, the presence of phytosterols in the sediment of Lake Oloiden marks a large outbreak of the freshwater fern *Salvinia molesta* and the increase of carotenoids shows the salination of the lake due to its separation from Lake Naivasha. In the case of Lake Naivasha, it is the start of floriculture and its impact on the lake. In the sediment of Lake Sonachi, the distributions of the carotenoids reflect a large freshwater influx into the lake which led to the formation of a well-defined silica layer. This layer also contained some unique markers.

Additionally, the long-chain *n*-alkanes, *n*-alkanols, and *n*-fatty acids characteristic for higher plants can be used to distinguish between different temperature regions in the Kenyan Rift (see fig. 4.11). In the lake sediments of the warmer northern region straight-chain compounds were on average longer than in the lake sediments of the cooler southern region.

It would certainly be useful to analyse the isotopic composition of the biomarkers found in the sediments. Those analyses might give information about climate changes, i.e. changes in precipitation, temperature, and vegetation, in the different areas.

The carotenoids found in this study reflected lake-level changes of Lake Bogoria as well as the salination of Lake Oloiden. This shows that, although those molecules are a diagenetic product, they are still very useful to reconstruct the history of the lakes. The hopanoids found in this study are more useful for diagenetic studies, since they are already strongly diagenetically altered.

The page features a minimalist design with three large blue circles and two thin blue lines. One circle is in the top right, a smaller one is in the middle right, and a large one is in the bottom right. Two thin blue lines run diagonally from the top left towards the middle right, framing the text.

## **Chapter 5:**

# **Summary, conclusions, and outlook**



## 5.1. Summary

The aim of this thesis was to study the hydrochemical and geochemical conditions in the sediment columns of seven Kenyan rift lakes. Those new-gained data sets were used to characterise the lake sediments, reconstruct the evolution of the single lakes, and to examine the influence of anthropogenic activities on the lake chemistry.

The analysis of the porewater revealed that the studied lakes can be put into three groups: 1) the two freshwater lakes (Lakes Baringo and Naivasha) with low salinities and moderate pH values (max. 450  $\mu\text{S}/\text{cm}$ ; pH 8), 2) Lakes Logipi, Eight, and Bogoria with high salinities and pH values (min. 41 000  $\mu\text{S}/\text{cm}$ ; pH  $\sim$  9.8), and 3) Lakes Oloiden and Sonachi which also had high pH values, but lower salinities than the second group (6 200 – 28 000  $\mu\text{S}/\text{cm}$ ). It was also observed that salinity and conductivity increased in south-northern direction as do temperature and evapotranspiration. The most dominant ions detected in the lakes' porewater include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$  (not detected in Lake Eight), and  $\text{SO}_4^{2-}$ . The single ion concentrations in the porewater profiles showed the same general trends with constant or downward increasing values in the core and lower values in the lake water. An exception was the porewater profile of Lake Naivasha which showed a pronounced zigzag trend that is probably related to unregulated water extraction rather than lake-level changes. Porewater analysis further revealed a possible zone of  $\text{NH}_4^+$  oxidation in the desiccation horizon of Lake Oloiden.

Sulphate-reduction rates (SRR) were highest in Lake Sonachi with 710  $\text{nmol}/(\text{cm}^3 \times \text{d})$  and lowest in Lake Baringo with 1.36  $\text{nmol}/(\text{cm}^3 \times \text{d})$ . In all studied lakes, SRR showed the characteristic hyperbolic curve; the only exception being Lake Naivasha where they followed the zigzag trend of  $\text{SO}_4^{2-}$  concentrations. Sulphate was only a limiting factor in the sediment of Lake Naivasha.

Horizons of elemental sulphur detected in the sediment cores of Lakes Logipi, Eight, Bogoria, and Sonachi correspond to time periods when the respective lake levels were significantly lower than today. This suggests that those horizons can be used as reliable markers for low lake levels in the past. Only in Lake Bogoria, AVS and CRS correlated with the lake level which might be related to a better preservation of those sulphur species due to the permanent stratification of the lake column.

Total biomarker concentrations were much higher in the three southern Lakes Naivasha, Oloiden, and Sonachi than in the two central ones (i.e. Lakes Baringo and Bogoria). The area around the southern lakes is densely populated and intensively used for agriculture which leads to a higher input of organic material. Additionally, the organic matter in Lake Baringo is diluted by a high sediment input, further decreasing the biomarker concentrations per depth interval. In all sediment cores, biomarker concentrations were highest at the top and decreased with depth. In Lake Bogoria, however, this profile followed lake-level changes because permanently anoxic bottom water favoured the preservation of biomarkers. The most important biomarkers detected in the lake sediments were straight-chain compounds (i.e. *n*-alkanes, *n*-alkanols, and *n*-fatty acids), hopanoids, and steroids.

Although the biomarker compositions of Lakes Baringo, Bogoria, Naivasha, Oloiden, and Sonachi were similar, there were some interesting and important differences. For example, almost completely saturated homologues of  $\beta$ -carotene were only detected in the saline lakes, because this molecule is probably derived from cyanobacteria populating the lakes. The origin of three short-chain *n*-alkanols (i.e. *n*-C<sub>15</sub>, *n*-C<sub>17</sub>, *n*-C<sub>19</sub>) and two sterenes remained unknown, but their occurrence was restricted to the saline lakes of this study. Stigmasterol was the only biomarker which was exclusively found in the two freshwater lakes. This sterol has its origin probably in freshwater algae, where it has often been reported.

In the sediment of Lake Naivasha, the biomarker distribution reflects the floricultural influence on the lake. Biomarkers increasing exponentially since the beginning of floriculture include the *n*-C<sub>17</sub> alkane, long-chain *n*-alkanes, phytosterols, and carboxylate esters. The increase of all those biomarkers, except long-chain *n*-alkanes, was attributed to increasing amounts of algae which multiplied due to higher inputs of fertilisers into the lake. The increase of long-chain *n*-alkanes was attributed to a larger input of plant material. In the sediment of Lake Oloiden, the influence from floriculture was not as pronounced as in the sediment of Lake Naivasha, but nevertheless present. The separation of Lake Oloiden from the main lake in the early 1980s was recorded in the distributions of the carotenoid isomers (i.e. the almost saturated homologues of  $\beta$ -carotene) and benzofuranones.

Distribution patterns of straight-chain compounds were dominated by long-chain compounds ranging from *n*-C<sub>23</sub> to *n*-C<sub>35</sub> due to the influence of higher plants and one or two short-chain compounds due to the influence of bacteria and/or algae. Odd-numbered *n*-alkanes and even-numbered *n*-alkanols and *n*-fatty acids were dominating the distributions. This kind of distribution pattern is expected of fresh and undegraded lake sediments. The only exceptions were the distributions of *n*-fatty acids from Lakes Oloiden and Sonachi where odd-numbered homologues were equally dominant and are likely associated with microbial reworking.

The ACLs of *n*-alkanes, *n*-alkanols, and *n*-fatty acids were generally high in all five lakes varying on average between 26.6 and 30.9 in the single sediment columns, which points to no major changes in input sources. It was observed that the  $ACL_{alk}$  and  $ACL_{FA}$  were higher in the sediment of the saline lakes than in the sediment of the two freshwater lakes which can be explained by vegetational differences in the catchment areas of the lakes, which also differ significantly in size.

It was observed that *cis* *n*-fatty acids were rapidly converted to their respective *trans* homologues in all sediment cores. *Cis* isomers were only detected in the sediment of Lake Naivasha due to a high *in situ* production. The saturation of short-chain *n*-fatty acids was independent of salinity or alkalinity and was much faster in Lakes Naivasha and Sonachi than, for example, in Lake Oloiden. The transformation of hopenes, on the other hand, seemed to be influenced by salinity and/or alkalinity, because a diagenetically more stable isomer was detected in the two freshwater Lakes Baringo and Naivasha (hop-17(21)-ene). In total, three hopene isomers were detected: hop-22(29)-ene, hop-21(22)-ene, and hop-17(21)-ene. The latter was not found in the saline Lakes Bogoria, Oloiden, and Sonachi. It is possible that the



salinity/alkalinity also has an influence on the isomer distributions. In Lake Naivasha, only one hop-22(29)-ene isomer was detected, whereas in the saline lakes a second isomer was detected which was also more abundant. It might, however, only be a coincidence. The hydrogenation of sterols in the sediments was always fast. The unsaturated cholesterol, for example, was only found in the upper sample, whereas the saturated counterpart  $\beta,\alpha$ -cholestanol was found throughout the sediment columns.

## 5.2. Conclusions

Based on the goals formulated at the beginning of this thesis (see subchapter 1.3), the obtained results led to the following main conclusions:

### *Is it possible to reconstruct the evolution of the lakes?*

The preservation of biomarkers in Lakes Bogoria and Sonachi was good due to the permanent stratification of the water column and anoxic bottom water, which slowed the degradation of organic matter. Consequently, those two lakes are the most useful ones to conduct environmental reconstructions based on biomarkers. Especially in Lake Bogoria, a large number of biomarkers can be used to reconstruct lake-level changes, e.g. long-chain *n*-alkanes and carotenoids (the isomers detected in this study). The other lakes are more problematic, because they are either strongly influenced by anthropogenic activities (floriculture around Lake Naivasha) or the organic matter was highly diluted due to a high sediment input (Lake Baringo). Nevertheless, some lakes possessed characteristic horizons which can be used as temporal markers. In Lakes Logipi, Eight, Bogoria, and Sonachi, distinct horizons of elemental sulphur are remnants of time periods when the respective lake levels were very low permitting anoxygenic photosynthesis (Lake Sonachi) or sulphide oxidation (Lakes Logipi, Eight, and Bogoria) to occur. The beginning of floriculture around Lake Naivasha was reflected in exponentially increasing concentrations of straight-chain compounds, phytosterols, and carboxylate esters. In Lake Oloiden, a 10 cm thick layer containing phytosterols coincides with a large outbreak of the freshwater fern *Salvinia molesta* in the early 1980s. Increasing carotenoid concentrations since this time reflect the salination of the lake due to its separation from Lake Naivasha. In the sediment of Lake Sonachi, the distributions of almost-completely saturated carotenoids reflect a large freshwater influx into the lake which led to the formation of a well-defined silica layer.

### *The influence of settlements, agriculture, and microorganisms on the lake chemistry*

The biomarker distribution in the sediment of Lake Naivasha, and to a certain extent also in the sediment of Lake Oloiden, is strongly influenced by the intensive growth of cut flowers in the

surrounding area. The distributions in the sediments of the other lakes were not influenced by anthropogenic activity, because they are neither intensively populated nor agriculturally used. Microorganisms also had a significant influence on the biomarker distributions of the sediments, but also on the porewater chemistry. Especially interesting in this regard, is the occurrence of anaerobic ammonium oxidation in the desiccation horizon of Lake Oloiden which led to elevated levels of nitrite, nitrate, and sulphate.

*Does lake chemistry influence the degradation of organic matter?*

Diagenetically more advanced isomers were found in Lakes Baringo and Naivasha which might indicate that the high salinity and/or alkalinity in the other lakes slow the transformation of hopenes. The degradation of all other studied biomarkers (i.e. *n*-fatty acids, sterols, carotenoids) was equally far developed in the single lakes independent of their salinity or alkalinity.

### **5.3. Outlook**

Future studies on those lakes should include a more detailed porewater profile of Lake Naivasha to see if the observed salinity fluctuations could be tied to lake-level changes. With the present profile, it was not possible to correlate it safely with former studies on lake-level fluctuations. It should also be investigated what hindered the cation measurement of the two freshwater Lakes Baringo and Naivasha. Lateral porewater profiles of the sediment should be made in order to exclude local phenomena, like it is probably the case in the sediment core from Lake Logipi, where water from a submerged hot spring seems to disturb the porewater. It would also be useful to analyse reduced sulphur species in the sediments of Lakes Baringo, Naivasha, and Oloiden, because this was not included in this study. This could also explain why no H<sub>2</sub>S was detected although sulphate reduction rates were high. In this context, iron concentrations in the sediments should be measured as well. It would also be interesting to study the microbial community in the sediment of Lake Naivasha to see if there are indeed two zones of microbial activity. It would also be useful to repeat the measurements of sulphate reduction rates with shorter incubation times, because the calculated rates in this study were too high. The biomarker distribution of Lake Bogoria should be studied in more detail, because of the lake's potential to record environmental changes. Isotope analyses might also be interesting, because they might tell us something about climatic changes (i.e. changes in precipitation, temperature, and vegetation) in more detail; especially where the biomarker composition was overprinted by anthropogenic or microbial activity.

The image features a minimalist abstract design on a white background. It consists of three solid black circles of varying sizes and three thin black lines. One large circle is positioned in the upper right quadrant, a smaller circle is centered below it, and a third large circle is partially visible at the bottom right corner. The lines are thin and intersect to form a triangular shape that encompasses the two upper circles. The word "Appendix" is printed in a bold, black, sans-serif font in the lower-left area of the page.

**Appendix**



**Appendix I: Chemical formulas**

<b>Br<sup>-</sup></b>	bromide	<b>MeOH</b>	methanol
<b>Ca<sup>2+</sup></b>	calcium cation	<b>Mg<sup>2+</sup></b>	magnesium cation
<b>Cl<sup>-</sup></b>	chloride	<b>N<sub>2</sub></b>	nitrogen gas
<b>CrCl<sub>2</sub></b>	chromous chloride	<b>Na<sup>+</sup></b>	sodium cation
<b>DCM</b>	dichloromethane	<b>Na<sub>2</sub>CO<sub>3</sub></b>	sodium carbonate
<b>DMF</b>	dimethylformamide	<b>NaCl</b>	sodium chloride
<b>F<sup>-</sup></b>	fluoride	<b>NH<sub>4</sub><sup>+</sup></b>	ammonium
<b>Fe<sup>2+</sup>/Fe<sup>3+</sup></b>	ferrous/ferric iron	<b>NO<sub>2</sub><sup>-</sup></b>	nitrate
<b>H<sub>2</sub>S</b>	hydrogen sulphide	<b>NO<sub>3</sub><sup>-</sup></b>	nitrate
<b>H<sub>2</sub>SO<sub>4</sub></b>	sulphuric acid	<b>PO<sub>4</sub><sup>3-</sup></b>	phosphate
<b>HCl</b>	hydrochloric acid	<b>SO<sub>4</sub><sup>2-</sup></b>	sulphate
<b>HCO<sub>3</sub><sup>-</sup></b>	hydrogen carbonate	<b>ZnAc</b>	zinc acetate
<b>K<sup>+</sup></b>	potassium cation	<b>ZnS</b>	zinc sulphide

**Appendix II: Abbreviations**

<b>ACL</b>	average chain length	<b>ITCZ</b>	Intertropical Convergence Zone
<b>ASE</b>	accelerated solvent extraction	<b>IUPAC</b>	International Union of Pure and Applied Chemistry
<b>AVS</b>	acid-volatile sulphur		
<b>b.l.f.</b>	below lake floor	<b>m.a.s.l.</b>	meter above sea level
<b>BW</b>	bottom water	<b>n.a.</b>	not attributed
<b>cpm</b>	counts per minute	<b>rpm</b>	rotations per minute
<b>CRS</b>	chromium-reducible sulphur	<b>SPE</b>	solid phase extraction
<b>dry wt.</b>	dry weight	<b>SRR</b>	sulphate reduction rates
<b>ES</b>	elemental sulphur	<b>SW</b>	surface water
<b>GC/MS</b>	gas chromatograph/mass spectrometry	<b>TRIS</b>	total reduced inorganic sulphur
		<b>WFB</b>	World Fact Book
<b>IC</b>	ion chromatography	<b>WHO</b>	World Health Organization

**Appendix III: List of figures**

- Figure 1.1** Topographical map of Kenya
- Figure 1.2** Climate and drainage system of the Kenyan Rift Valley
- Figure 1.3** Pictures of Lakes Logipi and Eight
- Figure 1.4** Pictures of Lakes Baringo and Bogoria
- Figure 1.5** Pictures of Lakes Oloiden and Sonachi
- Figure 1.6** Satellite images of the Kenyan lakes studied in this thesis
- Figure 2.1** Flow chart of the methodology
- Figure 3.1** Sulphur cycle
- Figure 3.2** Porewater and TRIS diagrams – Lake Logipi
- Figure 3.3** Porewater and TRIS diagrams – Lake Eight
- Figure 3.4** Porewater diagrams – Lake Baringo
- Figure 3.5** Biomarker diagrams – Lake Baringo
- Figure 3.6** Porewater and TRIS diagrams – Lake Bogoria
- Figure 3.7** Biomarker diagrams – Lake Bogoria
- Figure 3.8** Porewater diagrams – Lake Naivasha
- Figure 3.9** Biomarker diagrams – Lake Naivasha
- Figure 3.10** Porewater diagrams – Lake Oloiden
- Figure 3.11** Biomarker diagrams – Lake Oloiden
- Figure 3.12** Porewater and TRIS diagrams – Lake Sonachi
- Figure 3.13** Biomarker diagrams – Lake Sonachi
- Figure 4.1** Distributions of straight-chain compounds
- Figure 4.2** Diagrams: ACLs of straight-chain compounds
- Figure 4.3** Diagrams: Unsaturated/saturated short-chain *n*-fatty acids
- Figure 4.4** Diagenetic pathway of hop-22(29)-ene
- Figure 4.5** Diagrams: Relative amounts of different hopene isomers
- Figure 4.6** Diagram: hop-22(29)-ene/(17 $\alpha$ ,21 $\beta$ )-hopane in Lake Naivasha
- Figure 4.7** Phytosterols in the sediment of Lake Naivasha
- Figure 4.8**  $\beta$ -Carotene and its almost saturated form
- Figure 4.9** Diagenetic pathway of  $\beta$ -carotene
- Figure 4.10** Diagrams: carotenoids/dihydroactinidiolide
- Figure 4.11** Ternary diagrams of long-chain compounds

## **Appendix IV: List of tables**

<b>Table 2.1</b>	Dilution factors used for porewater analysis
<b>Table 2.2</b>	Analytical parameters for ion chromatography
<b>Table 2.3</b>	Overview of available data
<b>Table 3.1</b>	Biomarkers found in Lake Baringo sediments
<b>Table 3.2</b>	Biomarkers found in Lake Bogoria sediments
<b>Table 3.3</b>	Biomarkers found in Lake Naivasha sediments
<b>Table 3.4</b>	Biomarkers found in Lake Oloiden sediments
<b>Table 3.5</b>	Biomarkers found in Lake Sonachi sediments
<b>Table 4.1</b>	Lake water parameters of all lakes

## **Appendix V: Origin of photos and figures**

The photos of Lakes Logipi and Eight in figure 1.3 were a courtesy of Dr Annett Junginger. All other photos in this thesis were taken by myself during the field campaign in 2012.

The satellite images in figure 1.6 were taken from Google Maps (retrieved 14/12/2014).

The topographical map in figure 1.1 was modified after “Kenya Topography by Sadalmelik - own work” (licensed under Public Domain via Wikimedia Commons; retrieved 15/12/2014; [http://commons.wikimedia.org/wiki/File:Kenya\\_Topography.png#mediaviewer/File:Kenya\\_Topography.png](http://commons.wikimedia.org/wiki/File:Kenya_Topography.png#mediaviewer/File:Kenya_Topography.png)).

All other maps were created by myself using Mapcreator (Africa map in fig. 1.1) or QGIS (fig. 1.2, 1.6).

The sulphur cycle (fig. 3.1) was modified after “SKreislauf von Brudersohn - eigenes Werk” (licensed under CC BY-SA 3.0 via Wikimedia Commons; retrieved 04/02/2016; <https://commons.wikimedia.org/wiki/File:SKreislauf.png#/media/File:SKreislauf.png>).

Figures 4.4 and 4.9 were modified after Killops and Killops (2013).

All other figures were created by myself.

## Appendix VI: References

- Armstrong, G.A., Hearst, J.E., 1996. Carotenoids 2: Genetics and molecular biology of carotenoid pigment biosynthesis. *FASEB Journal* 10, 228–237.
- Åse, L.-E., 1987. A note on the water budget of Lake Naivasha, Kenya. Especially the role of *Salvinia Molesta* Mitch and *Cyperus papyrus* L. *Geografiska Annaler. Series A, Physical Geography* 69, 415–429. doi:10.2307/521355
- Åse, L.-E., Sernbo, K., 1986. Studies of Lake Naivasha, Kenya, and its drainage area. *Forskningsrapp./Stockholms univ. Naturgeografiska institutionen*.
- Baker, B.H., Wohlenberg, J., 1971. Structure and evolution of the Kenya Rift Valley. *Nature* 229, 538–542. doi:10.1038/229538a0
- Bauer, F.U., Glasmacher, U.A., Ring, U., Schumann, A., Nagudi, B., 2010. Thermal and exhumation history of the central Rwenzori Mountains, Western Rift of the East African Rift System, Uganda. *International Journal of Earth Sciences* 99, 1575–1597. doi:10.1007/s00531-010-0549-7
- Becht, R., Mwangi, F., Munro, F.A., 2006. Groundwater links between Kenyan Rift Valley lakes in “Proceedings of the 11th World Lakes Conference”, vol. 2, p. 7-14; editors: Odada, Eric & Olaga, Daniel O.
- Becht, R., Odada, E.O., Higgins, S., 2005. Lake Naivasha - Experience and lessons learned brief in “Managing lakes and their basins for sustainable use, a report for lake basin managers and stakeholders” for the International Lake Environment Committee Foundation (ILEC).
- Bergner, A.G.N., Strecker, M.R., Trauth, M.H., Deino, A., Gasse, F., Blisniuk, P., Dühnforth, M., 2009. Tectonic and climatic control on evolution of rift lakes in the Central Kenya Rift, East Africa. *Quaternary Science Reviews* 28, 2804–2816. doi:10.1016/j.quascirev.2009.07.008
- Bergner, A.G.N., Trauth, M.H., Bookhagen, B., 2003. Paleoprecipitation estimates for the Lake Naivasha Basin (Kenya) during the last 175 k.y. using a lake-balance model. *Global and Planetary Change* 36, 117–136. doi:10.1016/S0921-8181(02)00178-9
- Berner, R.A., 1970. Sedimentary pyrite formation. *American journal of science* 268, 1–23.
- Berner, R.A., Leeuw, J.W.D., Spiro, B., Murchison, D.G., Eglinton, G., 1985. Sulphate reduction, organic matter decomposition and pyrite formation [and discussion]. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 315, 25–38. doi:10.1098/rsta.1985.0027
- Bessems, I., Verschuren, D., Russell, J.M., Hus, J., Mees, F., Cumming, B.F., 2008. Palaeolimnological evidence for widespread late 18th century drought across equatorial East Africa. *Palaeogeography, Palaeoclimatology, Palaeoecology* 259, 107–120. doi:10.1016/j.palaeo.2007.10.002
- Bethell, P.H., Goad, L.J., Evershed, R.P., Ottaway, J., 1994. The study of molecular markers of human activity: The use of coprostanol in the soil as an indicator of human faecal material. *Journal of Archaeological Science* 21, 619–632.
- Bost, F., Frontera-Suau, R., McDonald, T., Peters, K., Morris, P., 2001. Aerobic biodegradation of hopanes and norhopanes in Venezuelan crude oils. *Organic Geochemistry* 32, 105–114.
- Bosworth, W., Maurin, A., 1993. Structure, geochronology and tectonic significance of the northern Suguta Valley (Gregory Rift), Kenya. *Journal of the Geological Society* 150, 751–762.
- Brink, A.B., Bodart, C., Buchanan, G., Clerici, M., Donnay, F., Eshiamwata, G., Gregoire, J.-M., Kirui, B.K., Lupi, A., Palumbo, I., Pekel, J.-F., 2013. Chapter 12 - Vegetation in “Paolo Paron, D.O.O. and C.T.O. (Ed.), *Developments in Earth Surface Processes, Kenya: A Natural Outlook Geo-Environmental Resources and Hazards*”. Elsevier, pp. 133–163.
- Brown, R.C., Wade, T.L., 1984. Sedimentary coprostanol and hydrocarbon distribution adjacent to a sewage outfall. *Water research* 18, 621–632.



- Burdige, D.J., Nealson, K.H., 1986. Chemical and microbiological studies of sulfide-mediated manganese reduction. *Geomicrobiology Journal* 4, 361–387.
- Burnett, G.W., Rowntree, K.M., 1990. Agriculture, research and tourism in the landscape of Lake Baringo, Kenya. *Landscape and Urban Planning, Interaction Between Local Populations and Protected Landscapes* 19, 159–172. doi:10.1016/0169-2046(90)90051-3
- Cardoso, J., Gaskell, S., Quirk, M., Eglinton, G., 1983. Hydrocarbon and fatty acid distributions in Rostherne Lake sediment (England). *Chemical Geology* 38, 107–128.
- Castanier, S., Bernet-Rollande, M.-C., Maurin, A., Perthuisot, J.-P., 1993. Effects of microbial activity on the hydrochemistry and sedimentology of Lake Logipi, Kenya in “Hurlbert, S.H. (Ed.), *Saline Lakes V, Developments in Hydrobiology*”. Springer Netherlands, pp. 99–112.
- Chorowicz, J., 2005. The East African Rift System. *Journal of African Earth Sciences, Phanerozoic Evolution of Africa* 43, 379–410. doi:10.1016/j.jafrearsci.2005.07.019
- Clément, J.-C., Shrestha, J., Ehrenfeld, J.G., Jaffé, P.R., 2005. Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils. *Soil Biology and Biochemistry* 37, 2323–2328.
- ClimateData.eu for precipitation and temperature data used for climate diagrams in fig. 1.2; the respective towns were chosen (<http://www.climatedata.eu/country.php?cc=ke&lang=en>; retrieved 13/04/2015).
- Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454–458. doi:10.4319/lo.1969.14.3.0454
- Cranwell, P., 1974. Monocarboxylic acids in lake sediments: Indicators, derived from terrestrial and aquatic biota, of paleoenvironmental trophic levels. *Chemical Geology* 14, 1–14.
- Cranwell, P., 1973. Chain-length distribution of *n*-alkanes from lake sediments in relation to post-glacial environmental change. *Freshwater Biology* 3, 259–265.
- Darling, W.G., Allen, D.J., Armannsson, H., 1990. Indirect detection of subsurface outflow from a rift valley lake. *Journal of Hydrology* 113, 297–306. doi:10.1016/0022-1694(90)90180-6
- Darling, W.G., Gizaw, B., Arusei, M.K., 1996. Lake-groundwater relationships and fluid-rock interaction in the East African Rift Valley: isotopic evidence. *Journal of African Earth Sciences, Hydrogeochemical Studies in Sub-Saharan Africa* 22, 423–431. doi:10.1016/0899-5362(96)00026-7
- Davies, T.C., 1996. Chemistry and pollution of natural waters in western Kenya. *Journal of African Earth Sciences, Environmental Geology of Kenya* 23, 547–563. doi:10.1016/S0899-5362(97)00018-3
- De Cort, G., Bessems, I., Keppens, E., Mees, F., Cumming, B., Verschuren, D., 2013. Late-Holocene and recent hydroclimatic variability in the central Kenya Rift Valley: The sediment record of hypersaline Lakes Bogoria, Nakuru and Elementeita. *Palaeogeography, Palaeoclimatology, Palaeoecology* 388, 69–80. doi:10.1016/j.palaeo.2013.07.029
- Dunkley, P., Smith, M., Allen, D.J., Darling, G., 1993. The geothermal activity and geology of the northern sector of the Kenya Rift Valley (Publication - Report). British Geological Survey Research Report SC/93/1.
- Dutka, B., Chau, A., Coburn, J., 1974. Relationship between bacterial indicators of water pollution and fecal sterols. *Water Research* 8, 1047–1055.
- Edwards, D.C., 1940. A vegetation map of Kenya with particular reference to grassland types. *Journal of Ecology* 28 (2), 377–385. doi:10.2307/2256235
- Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science* 156, 1322–1335.
- ElevationMap.net - Worldwide elevations; the respective towns were chosen (<http://elevationmap.net/#menu2>; retrieved 02/01/2015).

- Elvert, M., Whiticar, M., Suess, E., 2001. Diploptene in varved sediments of Saanich Inlet: Indicator of increasing bacterial activity under anaerobic conditions during the Holocene. *Marine Geology* 174, 371–383.
- Farrington, J.W., Quinn, J.G., 1971. Fatty acid diagenesis in recent sediment from Narragansett Bay, Rhode Island. *Nature* 230, 67–69.
- Fernandes, R.M.S., Ambrosius, B.A.C., Noomen, R., Bastos, L., Combrinck, L., Miranda, J.M., Spakman, W., 2004. Angular velocities of Nubia and Somalia from continuous GPS data: Implications on present-day relative kinematics. *Earth and Planetary Science Letters* 222, 197–208. doi:10.1016/j.epsl.2004.02.008
- Fossing, H., 1995. <sup>35</sup>S-radiolabeling to probe biogeochemical cycling of sulfur. *Geochemical Transformation of Sedimentary Sulfur*, p. 348-364.
- Foti, M., Sorokin, D.Y., Lomans, B., Mussman, M., Zacharova, E.E., Pimenov, N.V., Kuenen, J.G., Muyzer, G., 2007. Diversity, activity, and abundance of sulfate-reducing bacteria in saline and hypersaline soda lakes. *Applied and environmental microbiology* 73, 2093–2100.
- Fukushima, K., Ishiwatari, R., 1984. Acid and alcohol compositions of wax esters in sediments from different environments. *Chemical geology* 47, 41–56.
- Gaciri, S.J., Davies, T.C., 1993. The occurrence and geochemistry of fluoride in some natural waters of Kenya. *Journal of Hydrology* 143, 395–412. doi:10.1016/0022-1694(93)90201-J
- Gaskell, S.J., Eglinton, G., 1976. Sterols of a contemporary lacustrine sediment. *Geochimica et Cosmochimica Acta* 40, 1221–1228.
- Gaskell, S.J., Eglinton, G., 1975. Rapid hydrogenation of sterols in a contemporary lacustrine sediment. *Nature* 254, 209–211.
- Gaskell, S., Rhead, M., Brooks, P., Eglinton, G., 1976. Diagenesis of oleic acid in an estuarine sediment. *Chemical Geology* 17, 319–324.
- Gaudet, J.J., Melack, J.M., 1981. Major ion chemistry in a tropical African lake basin. *Freshwater Biology* 11, 309–333. doi:10.1111/j.1365-2427.1981.tb01264.x
- Gichora, M., Wittmann, D., Odulaja, A., 2001. Beekeeping in Baringo District, Kenya: Which way forward for research and extension? in "Proceedings of the 37th International Apicultural Congress", Durban South Africa.
- Gizaw, B., 1996. The origin of high bicarbonate and fluoride concentrations in waters of the Main Ethiopian Rift Valley, East African Rift System. *Journal of African Earth Sciences, Hydrogeochemical Studies in Sub-Saharan Africa* 22, 391–402. doi:10.1016/0899-5362(96)00029-2
- Google Earth - Lake extensions and canal connecting Lakes Naivasha and Oloiden (retrieved 14/12/2014 and 13/04/2015, respectively).
- Grimalt, J.O., Yruela, I., Sáiz-Jiménez, C., Toja, J., De Leeuw, J., Albaigés, J., 1991. Sedimentary lipid biogeochemistry of an hypereutrophic alkaline lagoon. *Geochimica et Cosmochimica Acta* 55, 2555–2577.
- Hackman, B.D., Charsley, T.J., Key, R.M., Wilkinson, A.F., 1990. The development of the East African Rift System in north-central Kenya. *Tectonophysics* 184, 189–211. doi:10.1016/0040-1951(90)90053-B
- Han, J., McCarthy, E.D., Van Hoesen, W., Calvin, M., Bradley, W., 1968. Organic geochemical studies, II. A preliminary report on the distribution of aliphatic hydrocarbons in algae, in bacteria, and in a recent lake sediment. *Proceedings of the National Academy of Sciences of the United States of America* 59, 29.
- Harped, D.M., Adams, C., Mavuti, K., 1995. The aquatic plant communities of the Lake Naivasha wetland, Kenya: Pattern, dynamics and conservation. *Wetlands Ecol Manage* 3, 111–123. doi:10.1007/BF00177693

- Harper, D., Mavuti, K.M., 2005. The ecological state of Lake Naivasha, Kenya, 2005: Turning 25 years research into an effective Ramsar monitoring programme. 11th World Lakes Conference KICC, Nairobi, Kenya.
- Harper, D.M., Childress, R.B., Harper, M.M., Boar, R.R., Hickley, P., Mills, S.C., Otieno, N., Drane, T., Vareschi, E., Nasirwa, O., Mwatha, W.E., Darlington, J.P.E.C., Escuté-Gasulla, X., 2003. Aquatic biodiversity and saline lakes: Lake Bogoria National Reserve, Kenya in "Martens, K. (Ed.), Aquatic Biodiversity, Developments in Hydrobiology". Springer Netherlands, pp. 259–276.
- Härtner, T., Straub, K.L., Kannenberg, E., 2005. Occurrence of hopanoid lipids in anaerobic *Geobacter* species. FEMS Microbiology Letters 243, 59–64.
- Hassett, J.P., Lee, G.F., 1977. Sterols in natural water and sediment. Water Research 11, 983–989.
- Hatcher, P.G., Simoneit, B.R., Mackenzie, F.T., Neumann, A.C., Thorstenson, D.C., Gerchakov, S.M., 1982. Organic geochemistry and pore water chemistry of sediments from Mangrove Lake, Bermuda. Organic Geochemistry 4, 93–112.
- Hinck, S., Neu, T.R., Lavik, G., Musmann, M., De Beer, D., Jonkers, H.M., 2007. Physiological adaptation of a nitrate-storing *Beggiatoa* sp. to diel cycling in a phototrophic hypersaline mat. Applied and environmental microbiology 73, 7013–7022.
- Hirschberg, J., Chamovitz, D., 1994. Carotenoids in cyanobacteria in "The Molecular Biology of Cyanobacteria". Springer, pp. 559–579.
- Hoffmann, B., Kahmen, A., Cernusak, L.A., Arndt, S.K., Sachse, D., 2013. Abundance and distribution of leaf wax *n*-alkanes in leaves of *Acacia* and *Eucalyptus* trees along a strong humidity gradient in northern Australia. Organic geochemistry 62, 62–67.
- Holmer, M., Storkholm, P., 2001. Sulphate reduction and sulphur cycling in lake sediments: A review. Freshwater Biology 46, 431–451.
- Hubble, D.S., Harper, D.M., 2002. Phytoplankton community structure and succession in the water column of Lake Naivasha, Kenya: A shallow tropical lake. Hydrobiologia 488, 89–98. doi:10.1023/A:1023314128188
- Hughen, K.A., Eglinton, T.I., Xu, L., Makou, M., 2004. Abrupt tropical vegetation response to rapid climate changes. Science 304, 1955–1959.
- Innes, H.E., Bishop, A.N., Fox, P.A., Head, I.M., Farrimond, P., 1998. Early diagenesis of bacteriohopanoids in recent sediments of Lake Pollen, Norway. Organic Geochemistry 29, 1285–1295.
- Ishiwatari, R., Hanya, T., 1975. Organic geochemistry of a 200-meter core sample from Lake Biwa. II. Proceedings of the Japan Academy 51, 436–441.
- Isoe, S., Hyeon, S.B., Sakan, T., 1969. Photo-oxygenation of carotenoids: I. The formation of dihydroactinidiolide and  $\beta$ -ionone from  $\beta$ -carotene. Tetrahedron Letters 10, 279–281.
- Jørgensen, B., 1978. A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments.
- Jørgensen, B.B., 1982. Mineralization of organic matter in the sea bed - The role of sulphate reduction. Nature 296, 643–645.
- Junginger, A., 2011. East African climate variability on different time scales - The Suguta Valley in the African-Asian Monsoon domain (Dissertation). Universität Potsdam, Germany.
- Junginger, A., Rohling, S., Kolß, S., Roller, S., Trauth, M.H., unpublished. Climate variability reconstruction of the past 150 years from the anthropogenic non-influenced Lake Eight in northern Kenya. Paleolimnology.
- Kallmeyer, J., Ferdelman, T.G., Weber, A., Fossing, H., Jørgensen, B.B., 2004. A cold chromium distillation procedure for radiolabeled sulfide applied to sulfate reduction measurements. Limnol. Oceanogr. Methods 2, 171–180. doi:10.4319/lom.2004.2.171

- Kawamura, K., Ishiwatari, R., 1985. Distribution of lipid-class compounds in bottom sediments of freshwater lakes with different trophic status, in Japan. *Chemical Geology* 51, 123–133.
- Kawamura, K., Ishiwatari, R., Ogura, K., 1987. Early diagenesis of organic matter in the water column and sediments: Microbial degradation and resynthesis of lipids in Lake Haruna. *Organic Geochemistry* 11, 251–264.
- Kenya Flower Council ([http://kenyaflowercouncil.org/?page\\_id=92](http://kenyaflowercouncil.org/?page_id=92); retrieved 14/11/2014).
- Kenya Open Data - Vol 1 A: Summary Population Distribution by District - 2009 (<https://www.opendata.go.ke/Population/Vol-1-A-Summary-Population-Distribution-by-District/jizy-xanw>; retrieved 24/11/2014).
- Kenyan Meteorological Department - The outlook for the March-April-May (MAM) 2015 “long rains” season in Kenya (Ref.no. KMD/FCST/5-2015/SO/01, issued 27/02/2015; retrieved 07/04/2015).
- Khoo, H.-E., Prasad, K.N., Kong, K.-W., Jiang, Y., Ismail, A., 2011. Carotenoids and their isomers: Color pigments in fruits and vegetables. *Molecules* 16, 1710–1738.
- Kilham, P., Hecky, R.E., 1973. Fluoride: Geochemical and ecological significance in East African waters and sediments. *Limnology and Oceanography* 18, 932–945.
- Killops, S.D., Killops, V.J., 2013. Introduction to organic geochemistry. John Wiley & Sons.
- Klok, J., Baas, M., Cox, H., De Leeuw, J., Schenck, P., 1984. Loliolides and dihydroactinidiolide in a recent marine sediment probably indicate a major transformation pathway of carotenoids. *Tetrahedron Letters* 25, 5577–5580.
- Kolattukudy, P., 1970. Plant waxes. *Lipids* 5, 259–275.
- Krienitz, L., Ballot, A., Kotut, K., Wiegand, C., Pütz, S., Metcalf, J.S., Codd, G.A., Stephan, P., 2003. Contribution of hot spring cyanobacteria to the mysterious deaths of Lesser Flamingos at Lake Bogoria, Kenya. *FEMS Microbiology Ecology* 43, 141–148.
- Kuria, Z., 2013. Groundwater distribution and aquifer characteristics in Kenya in “Kenya: A Natural Outlook Geo-Environmental Resources and Hazards” (1st ed). Elsevier.
- Kvenvolden, K.A., 1967. Normal fatty acids in sediments. *Journal of the American Oil Chemist's Society* 44, 628–636.
- Lambiase, J.J., Bosworth, W., 1995. Structural controls on sedimentation in continental rifts. Geological Society, London, Special Publications 80, 117–144. doi:10.1144/GSL.SP.1995.080.01.06
- Leavitt, P., Brown, S., 1988. Effects of grazing by *Daphnia* on algal carotenoids: Implications for paleolimnology. *Journal of Paleolimnology* 1, 201–213.
- Leavitt, P., Carpenter, S., 1990. Aphotic pigment degradation in the hypolimnion: Implications for sedimentation studies and paleolimnology. *Limnology and Oceanography* 35, 520–534.
- Library of Congress - Federal Research Division - Country profile Kenya (<http://lcweb2.loc.gov/frd/cs/profiles/Kenya.pdf>; retrieved 14/12/2014).
- Lichtfouse, E., Derenne, S., Mariotti, A., Largeau, C., 1994. Possible algal origin of long chain odd *n*-alkanes in immature sediments as revealed by distributions and carbon isotope ratios. *Organic Geochemistry* 22, 1023–1027.
- Logatchev, N.A., Belousov, V.V., Milanovsky, E.E., 1972. East African Rift development. *Tectonophysics, East Africa rifts* 15, 71–81. doi:10.1016/0040-1951(72)90053-4
- Lovley, D.R., Phillips, E.J., 1994. Novel processes for anaerobic sulfate production from elemental sulfur by sulfate-reducing bacteria. *Applied and Environmental Microbiology* 60, 2394–2399.
- Luther III, G.W., Popp, J.I., 2002. Kinetics of the abiotic reduction of polymeric manganese dioxide by nitrite: An anaerobic nitrification reaction. *Aquatic Geochemistry* 8, 15–36.

- Martins, C. de C., Fillmann, G., Montone, R.C., 2007. Natural and anthropogenic sterols inputs in surface sediments of Patos Lagoon, Brazil. *Journal of the Brazilian Chemical Society* 18, 106–115.
- Mathea, C.D., 2009. Our Lakes, Our Future in “13th World Lake Conference of the International Lake Environment Committee Foundation”, 01 - 05 November 2009, Wahun, China.
- Mathu, E.M., Davies, T.C., 1996. Geology and the environment in Kenya. *Journal of African Earth Sciences, Environmental Geology of Kenya* 23, 511–539. doi:10.1016/S0899-5362(97)00016-X
- Matsuda, H., 1978. Early diagenesis of fatty acids in lacustrine sediments - III. Changes in fatty acid composition in the sediments from a brackish water lake. *Geochimica et Cosmochimica Acta* 42, 1027–1034.
- Matsumoto, G.I., Akiyama, M., Watanuki, K., Torii, T., 1990. Unusual distributions of long-chain *n*-alkanes and *n*-alkenes in Antarctic soil. *Organic Geochemistry* 15, 403–412.
- Mavuti, K., Harper, D., 2006. The ecological state of Lake Naivasha, Kenya, 2005: Turning 25 years research into an effective Ramsar monitoring programme in “11th World Lakes Conference KICC”, Nairobi, Kenya.
- Mekonnen, M.M., Hoekstra, A.Y., Becht, R., 2012. Mitigating the water footprint of export cut flowers from the Lake Naivasha Basin, Kenya. *Water Resour Manage* 26, 3725–3742. doi:10.1007/s11269-012-0099-9
- Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry - An overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic geochemistry* 20, 867–900.
- Mohanakrishnan, J., Gutierrez, O., Sharma, K.R., Guisasola, A., Werner, U., Meyer, R.L., Keller, J., Yuan, Z., 2009. Impact of nitrate addition on biofilm properties and activities in rising main sewers. *Water research* 43, 4225–4237.
- Nanyaro, J.T., Aswathanarayana, U., Mungure, J.S., Lahermo, P.W., 1984. A geochemical model for the abnormal fluoride concentrations in waters in parts of northern Tanzania. *Journal of African Earth Sciences* 2, 129–140. doi:10.1016/S0731-7247(84)80007-5
- Neukirchen, F., 2004. Stratigraphie und Petrologie der Lavenabfolge in der Bruchstufe zwischen Oldoinyo Lengai und Engare Sero Canyon, Tansania (Diplomarbeit). Freiburg, Germany.
- Nicholson, S.E., 1998. Historical fluctuations of Lake Victoria and other lakes in the northern Rift Valley of East Africa in “Environmental Change and Response in East African Lakes”. Springer, pp. 7–35.
- Nicholson, S.E., 1996. A review of climate dynamics and climate variability in Eastern Africa. CRC Press.
- Nishimura, M., 1982. 5 $\beta$ -Isomers of stanols and stanones as potential markers of sedimentary organic quality and depositional paleoenvironments. *Geochimica et Cosmochimica Acta* 46, 423–432.
- Nishimura, M., Baker, E.W., 1986. Possible origin of *n*-alkanes with a remarkable even-to-odd predominance in recent marine sediments. *Geochimica et Cosmochimica Acta* 50, 299–305.
- Nishimura, M., Koyama, T., 1976. Stenols and stanols in lake sediments and diatoms. *Chemical Geology* 17, 229–239.
- Nunn, J.A., Harris, N.B., 2007. Subsurface seepage of seawater across a barrier: A source of water and salt to peripheral salt basins. *Geological Society of America Bulletin* 119, 1201–1217. doi:10.1130/B26088.1
- Odada, E., Onyando, J., Obudho, P., 2005. Lake Baringo - Experience and lessons learned brief in “Managing lakes and their basins for sustainable use, a report for lake basin managers and stakeholders” for the International Lake Environment Committee Foundation (ILEC).

- Oduor, S.O., Schagerl, M., Mathooko, J.M., 2003. On the limnology of Lake Baringo (Kenya): I. Temporal physico-chemical dynamics. *Hydrobiologia* 506-509, 121–127. doi:10.1023/B:HYDR.0000008563.00000.18
- Oduor, S., Schagerl, M., 2007. Phytoplankton primary productivity characteristics in response to photosynthetically active radiation in three Kenyan Rift Valley saline–alkaline lakes. *Journal of Plankton Research* 29, 1041–1050.
- Ojiambo, B.S., Poreda, R.J., Lyons, W.B., 2001. Ground water/surface water interactions in Lake Naivasha, Kenya, using  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ , and  $^3\text{H}/^3\text{He}$  age-dating. *Ground Water* 39, 526–533. doi:10.1111/j.1745-6584.2001.tb02341.x
- Olaka, L.A., Odada, E.O., Trauth, M.H., Olago, D.O., 2010. The sensitivity of East African rift lakes to climate fluctuations. *J Paleolimnol* 44, 629–644. doi:10.1007/s10933-010-9442-4
- Otiang’ a-Owiti, G.E., Oswe, I.A., 2007. Human impact on lake ecosystems: The case of Lake Naivasha, Kenya. *African Journal of Aquatic Science* 32, 79–88. doi:10.2989/AJAS.2007.32.1.11.148
- Pickford, M., 1994. Patterns of sedimentation and fossil distribution in the Kenya Rift Valleys. *Journal of African Earth Sciences* 18, 51–60. doi:10.1016/0899-5362(94)90053-1
- Pickford, M., 1990. Uplift of the roof of Africa and its bearing on the evolution of mankind. *Hum. Evol.* 5, 1–20. doi:10.1007/BF02436472
- Prince, R.C., Elmendorf, D.L., Lute, J.R., Hsu, C.S., Haith, C.E., Senius, J.D., Dechert, G.J., Douglas, G.S., Butler, E.L., 1994.  $17\alpha(\text{H}), 21\beta(\text{H})$ -Hopane as a conserved internal marker for estimating the biodegradation of crude oil. *Environmental Science & Technology* 28, 142–145.
- Renaut, R.W., Jones, B., Tiercelin, J.-J., 1998. Rapid *in situ* silicification of microbes at Loburu hot springs, Lake Bogoria, Kenya Rift Valley. *Sedimentology* 45, 1083–1103. doi:10.1046/j.1365-3091.1998.00194.x
- Renaut, R.W., Jones, B., Tiercelin, J.-J., Tarits, C., 2002. Sublacustrine precipitation of hydrothermal silica in rift lakes: Evidence from Lake Baringo, central Kenya Rift Valley. *Sedimentary Geology* 148, 235–257. doi:10.1016/S0037-0738(01)00220-2
- Renaut, R.W., Owen, R.B., 1988. Opaline cherts associated with sublacustrine hydrothermal springs at Lake Bogoria, Kenya Rift Valley. *Geology* 16, 699–702. doi:10.1130/0091-7613(1988)016<0699:OCAWSH>2.3.CO;2
- Renaut, R.W., Tiercelin, J.-J., 1993. Lake Bogoria, Kenya: Soda, hot springs and about a million flamingoes. *Geology Today* 9, 56–61. doi:10.1111/j.1365-2451.1993.tb00981.x
- Rhemtulla, S., 1970. The South Turkana expedition: Scientific Papers III. A geological reconnaissance of South Turkana. *The Geographical Journal* 136, 61–73. doi:10.2307/1795682
- Rielley, G., Collier, R., Jones, D., Eglinton, G., 1991. The biogeochemistry of Ellesmere Lake, UK - I: Source correlation of leaf wax inputs to the sedimentary lipid record. *Organic Geochemistry* 17, 901–912.
- Rohmer, M., Bouvier-Nave, P., Ourisson, G., 1984. Distribution of hopanoid triterpenes in prokaryotes. *Microbiology* 130, 1137–1150.
- Rommerskirchen, F., Eglinton, G., Dupont, L., Rullkötter, J., 2006. Glacial/interglacial changes in southern Africa: Compound-specific  $\delta^{13}\text{C}$  land plant biomarker and pollen records from southeast Atlantic continental margin sediments. *Geochemistry, Geophysics, Geosystems* 7. doi:10.1029/2005GC001223
- Rudd, J.W.M., Kelly, C.A., Furutani, A., 1986. The role of sulfate reduction in long term accumulation of organic and inorganic sulfur in lake sediments. *Limnol. Oceanogr.* 31, 1281–1291. doi:10.4319/lo.1986.31.6.1281
- Sachse, D., Radke, J., Gleixner, G., 2006.  $\delta\text{D}$  values of individual *n*-alkanes from terrestrial plants along a climatic gradient - Implications for the sedimentary biomarker record. *Organic Geochemistry* 37, 469–483.

- Schefuß, E., Ratmeyer, V., Stuet, J.-B.W., Jansen, J.F., Damsté, J.S.S., 2003. Carbon isotope analyses of *n*-alkanes in dust from the lower atmosphere over the central eastern Atlantic. *Geochimica et Cosmochimica Acta* 67, 1757–1767.
- Schieber, A., Carle, R., 2005. Occurrence of carotenoid *cis*-isomers in food: Technological, analytical, and nutritional implications. *Trends in Food Science & Technology* 16, 416–422.
- Schippers, A., Jørgensen, B., 2001. Oxidation of pyrite and iron sulfide by manganese dioxide in marine sediments. *Geochimica et Cosmochimica Acta* 65, 915–922.
- Schippers, A., Jørgensen, B.B., 2002. Biogeochemistry of pyrite and iron sulfide oxidation in marine sediments. *Geochimica et Cosmochimica Acta* 66, 85–92.
- Schmidt, T.M., Arieli, B., Cohen, Y., Padan, E., Strohl, W.R., 1987. Sulfur metabolism in *Beggiatoa alba*. *J. Bacteriol.* 169, 5466–5472.
- Schneider, D., 2013. Metagenomic and metatranscriptomic analyses of calcifying biofilms (Dissertation). Georg-August-Universität Göttingen, Germany.
- Schouten, S., Rijpstra, W., Kok, M., Hopmans, E., Summons, R., Volkman, J., Damsté, J.S., 2001. Molecular organic tracers of biogeochemical processes in a saline meromictic lake (Ace Lake). *Geochimica et Cosmochimica Acta* 65, 1629–1640.
- Seguel, C.G., Mudge, S.M., Salgado, C., Toledo, M., 2001. Tracing sewage in the marine environment: Altered signatures in Concepción Bay, Chile. *Water Research* 35, 4166–4174.
- Simoneit, B.R., 2005. A review of current applications of mass spectrometry for biomarker/molecular tracer elucidations. *Mass Spectrometry Reviews* 24, 719–765.
- Singh, A., Diop, S., M'mayi, P.L., 2006. Africa's Lakes: Atlas of our changing environment. UNEP/Earthprint.
- Smith, M., 1994. Stratigraphic and structural constraints on mechanisms of active rifting in the Gregory Rift, Kenya. *Tectonophysics, Crustal and upper mantle structure of the Kenya Rift* 236, 3–22. doi:10.1016/0040-1951(94)90166-X
- Stoof-Leichsenring, K.R., Junginger, A., Olaka, L.A., Tiedemann, R., Trauth, M.H., 2011. Environmental variability in Lake Naivasha, Kenya, over the last two centuries. *J Paleolimnol* 45, 353–367. doi:10.1007/s10933-011-9502-4
- Sun, M.-Y., Wakeham, S.G., Lee, C., 1997. Rates and mechanisms of fatty acid degradation in oxic and anoxic coastal marine sediments of Long Island Sound, New York, USA. *Geochimica et Cosmochimica Acta* 61, 341–355.
- Tarits, C., Renaut, R.W., Tiercelin, J.-J., Le Hérisse, A., Cotten, J., Cabon, J.-Y., 2006. Geochemical evidence of hydrothermal recharge in Lake Baringo, central Kenya Rift Valley. *Hydrol. Process.* 20, 2027–2055. doi:10.1002/hyp.6046
- Tarras-Wahlberg, H., Everard, M., Harper, D.M., 2002. Geochemical and physical characteristics of river and lake sediments at Naivasha, Kenya. *Hydrobiologia* 488, 27–41.
- Tarras-Wahlberg, N., 1986. Observations on *Salvinia* and its environment at Lake Naivasha (Kenya). *Journal of East African natural history*. Vol. 76, No. 189, 1–8.
- Tea Board of Kenya (<http://www.teaboard.or.ke/statistics/exports.html>; retrieved 14/11/2014).
- The World Factbook - Kenya, Central Intelligence Agency, Washington, D.C. (<https://www.cia.gov/library/publications/the-world-factbook/geos/ke.html>; retrieved 09/01/2015).
- Tiercelin, J.-J., Vincens, A., Barton, C., 1987. Le demi-graben de Baringo-Bogoria, Rift Gregory, Kenya: 30 000 ans d'histoire hydrologique et sédimentaire. *Soc. Nat. Elf Aquitaine*.
- Tipple, B.J., Pagani, M., 2013. Environmental control on eastern broadleaf forest species' leaf wax distributions and D/H ratios. *Geochimica et Cosmochimica Acta* 111, 64–77.
- Uku, J.N., Mavuti, K.M., 1994. Comparative limnology, species diversity and biomass relationship of zooplankton and phytoplankton in five freshwater lakes in Kenya. *Hydrobiologia* 272, 251–258. doi:10.1007/BF00006525

- UNESCO World Heritage Centre - Lake Bogoria National Reserve, 1999 (<http://whc.unesco.org/en/tentativelists/1346/>; retrieved 11/04/2015).
- Van Vleet, E.S., Quinn, J.G., 1976. Characterisation of monounsaturated fatty acids from an estuarine sediment. *Nature* 262, 126-128.
- Verschuren, D., 2003. Lake-based climate reconstruction in Africa: progress and challenges in "Martens, K. (Ed.), *Aquatic Biodiversity, Developments in Hydrobiology*". Springer Netherlands, pp. 315–330.
- Verschuren, D., 2001. Reconstructing fluctuations of a shallow East African lake during the past 1800 yrs from sediment stratigraphy in a submerged crater basin. *Journal of Paleolimnology* 25, 297–311. doi:10.1023/A:1011150300252
- Verschuren, D., 1999a. Influence of depth and mixing regime on sedimentation in a small, fluctuating tropical soda lake. *Limnol. Oceanogr.* 44, 1103–1113. doi:10.4319/lo.1999.44.4.1103
- Verschuren, D., 1999b. Sedimentation controls on the preservation and time resolution of climate-proxy records from shallow fluctuating lakes. *Quaternary Science Reviews* 18, 821–837. doi:10.1016/S0277-3791(98)00065-1
- Verschuren, D., 1994. Sensitivity of tropical-African aquatic invertebrates to short-term trends in lake level and salinity: A paleolimnological test at Lake Oloidien, Kenya. *Journal of Paleolimnology* 10, 253–263.
- Verschuren, D., Cocquyt, C., Tibby, J., Roberts, C.N., Leavitt, P.R., 1999a. Long-term dynamics of algal and invertebrate communities in a small, fluctuating tropical soda lake. *Limnol. Oceanogr.* 44, 1216–1231. doi:10.4319/lo.1999.44.5.1216
- Verschuren, D., Laird, K.R., Cumming, B.F., 2000. Rainfall and drought in equatorial East Africa during the past 1,100 years. *Nature* 403, 410–414. doi:10.1038/35000179
- Verschuren, D., Tibby, J., Leavitt, P.R., Roberts, C.N., 1999b. The environmental history of a climate-sensitive lake in the former "White Highlands" of central Kenya. *AMBIO* 28, 494–501.
- Volcanoes of the World - Alphabetic list from A-Z (<http://www.volcanodiscovery.com/volcanoes/alphabetical-list/a-z.html>; retrieved 07/04/2015).
- Volkman, J., 2003. Sterols in microorganisms. *Applied microbiology and Biotechnology* 60, 495–506.
- Volkman, J., Johns, R., Gillan, F., Perry, G., Bavor, H., 1980. Microbial lipids of an intertidal sediment - I. Fatty acids and hydrocarbons. *Geochimica et Cosmochimica Acta* 44, 1133–1143.
- Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry* 9, 83–99.
- Wang, N., Zong, Y., Brodie, C.R., Zheng, Z., 2014. An examination of the fidelity of *n*-alkanes as a palaeoclimate proxy from sediments of Palaeolake Tianyang, South China. *Quaternary International* 333, 100–109.
- Wen-Yen, H., Meinschein, W., 1976. Sterols as source indicators of organic materials in sediments. *Geochimica et Cosmochimica Acta* 40, 323–330.
- World Health Organization (WHO) - Fluoride ([http://www.who.int/water\\_sanitation\\_health/dwq/nutfluoride/en/](http://www.who.int/water_sanitation_health/dwq/nutfluoride/en/); retrieved 03/02/2015).
- World Health Organization (WHO) - Fluorides (EHC 227, 2002; <http://www.inchem.org/documents/ehc/ehc/ehc227.htm#1.4> (retrieved 02/11/2015)).