



# Distributions and compound-specific isotopic signatures of sedimentary chlorins reflect the composition of photoautotrophic communities and their carbon and nitrogen sources in Swiss lakes and the Black Sea



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## ABSTRACT

We examined the distributions of tetrapyrrole pigments (i.e. intact chlorophylls and bacteriochlorophylls, pheopigments) as well as their compound-specific carbon and nitrogen isotopic compositions in the sediments of three Swiss lakes (Lakes Rotsee, Cadagno and Zurich) and the Black Sea to investigate the biogeochemical cycling of carbon and nitrogen mediated by phototrophic eukaryotes (algae) and bacteria. The factors controlling chlorin isotope variations are discussed and the feasibility to use chlorins as indicators for reconstructions of surface water environments is evaluated. Chlorophyll *a* and its derivatives including pheophytin *a*, a pheophytin *a* epimer, pyropheophytin *a*, 13<sup>2</sup>,17<sup>3</sup>-cyclophosphoribide-*a*-enol, chlorophyllone *a* as well as steryl and carotenol chlorin esters were detected in all sediments. The presence of bacteriochlorophylls *e* and their derivatives confirmed the presence of brown strains of green phototrophic sulfur bacteria (*Chlorobiaceae*; GSB) in all three lakes. In the shallower Lakes Rotsee and Cadagno, purple sulfur bacteria (*Chromatiaceae*; PSB) were also present as confirmed by bacteriochlorophyll *a* derivatives. Despite the different degrees of water column hypoxia at the studied sites, the chlorins in all sediments were attributed to rapid transformation of intact tetrapyrroles and the formation of related pheopigments. The scatter of compound-specific carbon isotopic compositions of Chl *a* and its derivatives resulted from different timing of pheopigment formation, likely due to the interaction of blooms of various phytoplankton communities at different times of the year and the variable degrees of carbon limitation and/or different contributions of recycled organic matter (OM). The nitrogen isotopic composition of the chloropigments mainly derived from nitrate assimilation in Lake Zurich and the Black Sea, whereas ammonium and nitrate assimilation were predominant in Lake Rotsee. In the epilimnion of the meromictic Lake Cadagno, dissolved organic nitrogen (DON) supplied to the surface water from ammonium assimilation in the chemocline may be the main nitrogen source. Phototrophic sulfur bacteria in Lakes Rotsee and Cadagno thrived mainly under dissolved organic carbon depleted conditions within the chemocline and in the hypolimnion. GSB may use predominantly ammonium and at least in Lake Cadagno also perform N<sub>2</sub> fixation. In contrast, the nitrogen source of PSB could not be reconstructed with δ<sup>15</sup>N values of bacteriochlorins, because nitrogen isotopic fractionation during BChl *a* synthesis seems to be almost independent of the assimilated substrate.

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## 1. Introduction

Chlorophylls and bacteriochlorophylls are the essential pigments for oxygenic and anoxygenic photosynthesis, respectively, and represent

the most abundant pigments on Earth (Falkowski, 2003; Keely, 2006; Scheer, 2006). Accordingly, chlorophyll *a* (Chl *a*; Fig. A.1) is ubiquitous and the predominant pigment in eukaryotic photoautotrophs and cyanobacteria from both marine and terrestrial environments (e.g. Scheer, 2006). In contrast, bacteriochlorophylls are the main pigments of phototrophic bacteria in aquatic environments to capture electromagnetic radiation (e.g. Pfennig, 1978). Phototrophic bacteria such as *Chromatiaceae* (purple phototrophic sulfur bacteria; PSB) and *Chlorobiaceae* (green phototrophic sulfur bacteria; GSB) thrive under euxinic (free H<sub>2</sub>S) conditions in the photic zone (e.g. Pfennig, 1978).

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While GSB are obligate anaerobes, PSB are facultative anaerobes (e.g. Pfennig, 1978).

Chlorophylls and bacteriochlorophylls are transformed to a large variety of degradation products, including pheopigments, porphyrins and maleimides (e.g. Hodgson et al., 1968; Grice et al., 1996; Keely, 2006; Louda et al., 2011). These compounds are formed within living or senescent cells, in the water column and during sedimentation (e.g. Barwise and Roberts, 1984; Bianchi et al., 1993; Louda et al., 1998, 2011). The underlying processes are autolytic degradation, photochemical, enzymatic and hydrolytic reactions, microbial or viral lysis and grazing (e.g. Owens and Falkowski, 1982; Gossauer and Engel, 1996; Louda et al., 1998; Chen et al., 2003).

Primary degradation products of chlorophylls include pheophytins, pheophorbides and pyropheophytins, which are formed by demetalation of the central Mg ion, by ester hydrolysis and by demethoxy-carbonylation, respectively (e.g. Chen et al., 2003; Keely, 2006). Furthermore, they include 13<sup>2</sup>,17<sup>3</sup>-cyclophorbide-*a*-enol (CPhe *a*; Fig. A.1), which has been considered to be formed by grazing (Goericke et al., 2000), but can also be derived from pyropheophorbide *a* within the sediment (Louda et al., 2000). Other derivatives are steryl and carotenol chlorin esters (SCEs and CCEs; Fig. A.1), esterified products of secondary reactions of tetrapyrroles with steroids or carotenoids, respectively (e.g. Furlong and Carpenter, 1988; King and Repeta, 1991; Spooner et al., 1994; Harradine et al., 1996; Chen et al., 2003).

Despite of these various alterations, which can occur on timescales of hours to days or weeks and continue in the sediment (Owens and Falkowski, 1982; SooHoo and Kiefer, 1982; Furlong and Carpenter, 1988; Bianchi et al., 1993; Sun et al., 1993; Goericke et al., 2000), these tetrapyrroles and their degradation products in the sedimentary record provide evidence of all photoautotrophic communities in the water column together with carotenoids (e.g. Züllig, 1985; Keely, 2006).

The preservation of the tetrapyrrole macrocycle facilitates unique biogeochemical reconstructions, as the carbon and nitrogen isotopic signatures are expected to be only minimally altered during diagenesis. This is valuable for the reconstruction of surface water environments, the composition of phototrophic communities and the biogeochemical cycling of carbon and nitrogen (Macko and Estep, 1984; Ohkouchi et al., 2005, 2006; Ohkouchi and Takano, 2014; e.g. Sachs et al., 1999; Tyler et al., 2010). Specifically, the bulk nitrogen isotopic composition is prone to significant alteration during diagenesis (e.g. Sigman et al., 1999; Freudenthal et al., 2001; Lehmann et al., 2002; Robinson et al., 2012), whereas nitrogen within the tetrapyrrole ring in chlorophylls and their derivatives remains unaffected (e.g. Sachs et al., 1999; Tyler et al., 2010; Higgins et al., 2011). Moreover, the inherent heterogeneity of bulk OM, as it is derived from various sources (i.e. bacteria and eukaryotes), prevents specific interpretations of phytoplankton communities. Therefore, the compound-specific isotope analysis of photosynthetic pigments provide a tool to delineate biogeochemical processes of distinct community assemblages in surface water environments (e.g. Hayes et al., 1990; Ohkouchi et al., 2005; Tyler et al., 2010).

Recent developments in analytical techniques have enhanced chlorin purification using high performance liquid chromatography (HPLC) (Sachs and Repeta, 2000; Higgins et al., 2009) and the analysis of carbon and nitrogen isotopic signatures by sensitivity-improved isotope-ratio mass spectrometry (Polissar et al., 2009; Ogawa et al., 2010). However, only a small number of studies have explored the high potential of isotopic signatures of chlorins to better understand how different phototrophic assemblages mediate the biogeochemical cycling of carbon and nitrogen in oxygen rich and oxygen deficient aquatic environments and how environmental factors control isotopic signatures in tetrapyrroles (summarised by Ohkouchi and Takano, 2014). The underlying processes that lead to the observed stable isotope compositions of chlorins are still barely understood, especially in lakes with different biogeochemical characteristics (i.e. oxygen content, stratification, nutrient availability, phototrophic community assemblages).

Here, we analysed compound-specific carbon and nitrogen isotopic compositions of tetrapyrrole pigments (chlorophylls, bacteriochlorophylls, and related pheopigments) in the sediments of three Swiss lakes (Lakes Rotsee, Cadagno and Zurich) and the Black Sea (Romanian Shelf) to investigate the role of phototrophic algae and bacteria in the biogeochemical cycling of carbon and nitrogen in these systems. We discuss the impact of degradation on pigment distributions, factors that control variations in the stable isotope composition of isolated chlorins and evaluate their feasibility to reconstruct nitrogen sources of the phototrophic communities.

## 2. Material and methods

### 2.1. Study sites and sample collection

Lake Zurich (Lower Lake area of 67.3 km<sup>2</sup>) is a prealpine, mesotrophic, either monomictic or dimictic lake depending on prevailing winter conditions. The surface sediment sample (0–2 cm) studied originates from a 110 cm long core (ZH-09-05) obtained with a gravity corer at the maximum depth of 137 m in November 2009 (47°17.004'N, 8°35.640'E, WGS84). The average sedimentation rate in the varved section of this core is ca. 0.28 cm yr<sup>-1</sup>, identical with estimates on an equivalent core from the same site that has been studied previously (Naeher et al., 2013a). In this lake, non-N<sub>2</sub>-fixing cyanobacterium *Planktothrix rubescens* ("burgundy blood algae") has become the dominant species during the past four decades as a result of reoligotrophication due to the associated decrease in phosphate concentrations and warmer water temperatures (Posch et al., 2012). From September to March *P. rubescens* alone represents more than 50% of the total phytoplankton biomass (Bossard et al., 2001). Co-dominating algae in the lake are diatoms and *Cryptophyceae*, whereas chlorophyta account for less than 10% of phytoplankton biomass (Bossard et al., 2001).

Lake Rotsee is a small (0.46 km<sup>2</sup>) prealpine, monomictic and eutrophic lake. The lake has a stable stratified water column with a strong chemocline between ca. 6 and 10 m depth and an anoxic hypolimnion for most of the year (Schubert et al., 2010). In this study we use surface sediment (0–4 cm) from a 65 cm long core (Rot-10-3) obtained with a gravity corer at the maximum depth of 16 m in August 2010 (47°4.251'N, 8°18.955'E, WGS84). Naeher et al. (2012) reported the average sedimentation rate of ca. 0.38 cm yr<sup>-1</sup>. The lake has a high species richness and diversity with *Cryptophyceae*, *Chlorophyceae* and diatoms being the predominant algae. Cyanobacteria (mainly *P. rubescens*) present in the surface water are only more abundant than algae during blooms in fall, whereas diatoms dominate at about 5–7 m water depth (monitoring data of the Cantonal Office of Environment and Energy; F. Schanz personal communication). N<sub>2</sub> fixing cyanobacteria are low in abundance (monitoring data of the Cantonal Office of Environment and Energy; F. Schanz personal communication). Also purple and green phototrophic sulfur bacteria (PSB, GSB) are present (e.g. Kohler et al., 1984; Züllig, 1985).

Lake Cadagno is a small (0.26 km<sup>2</sup>), alpine, mesotrophic and meromictic lake. The lake has a strong chemocline between ca. 10 and 13 m and is permanently stratified (Wirth et al., 2013). A sediment core was collected from the deepest part of the lake (21 m depth) in September 2009 (46°33.000'N, 8°42.000'E, WGS84; Wirth et al., 2013) using an UWITEC platform with a percussion piston-coring system. The surface sediment is not available, and we used a sediment sample with a depth of 633–638 cm of the core, which corresponds to 5000–5600 calendar years before present (cal yr BP) based on the radiocarbon dates. The sedimentation rate is ca. 2 mm yr<sup>-1</sup> (Wirth et al., 2013). In Lake Cadagno, phytoplanktonic communities are dominated by green algae (predominant chlorophyte: *Echinocoleum elegans*), diatoms, cryptophytes and dinophytes in early summer, with increasing abundances of diatoms, followed by green algae and flagellates towards late summer (Schanz and Stalder, 1998; Bossard et al., 2001). PSB and

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