

WHAT CAN A FJORD IN NORWAY TELL US ABOUT CARBON CYCLE CHANGES DURING NATURAL GREEN-HOUSE CONDITIONS IN THE EARTH HISTORY?

*Yvonne van Breugel, Mathias Paetzel, Stefan Schouten & Jaap Sinninghe Damsté**

Massive combustion of fossil fuel by man since the industrial revolution has increased the atmospheric CO₂ levels from 280 ppmv (parts per million by volume) in 1800 to about 376 ppmv in 2004. To understand what might be ahead of us, we have to look back in the earth history to earlier periods with natural green house conditions. These occurred 180 million years ago in the Jurassic and 120 million years ago in the Cretaceous during so called “oceanic anoxic events” (OAE’s). A striking feature of both periods is the extent of oxygen depletion in the world’s oceans. Since the present day situation in some Norwegian fjords presents similar environmental conditions, we investigated the carbon cycle in the Kyllaren fjord. This fjord has a stratified water column year round with a very shallow chemocline at 3.5 m depth. Our results show that respired CO₂ from re-mineralized cellular material accumulates below the chemocline and is used as a ‘second-hand’ carbon-source by the green sulphur bacteria, living at 4 m depth in Kyllaren fjord. We think that the recycling of respired CO₂ was also a very important process in the ancient (shallow) oceans during both pre-historical ocean anoxic events.

50

The OAE’s in the Jurassic (180 Ma) and in the Cretaceous (120 Ma) are characterized by large volcanic activities, causing elevated atmospheric CO₂ levels and high temperatures. Another striking feature during both periods was the lack of oxygen in the bottom water of the oceans, sometimes even up into the photic zone (where light penetrates in the water). In our present day oceans, all bottom water is oxygenated. The Kyllaren fjord (Fig. 1), however, is anoxic below 3.5 m depth. The 29-meter deep fjord is located on the west coast of Norway and is connected with the Norwegian Sea by a nar-

row, 1-2 m deep channel. Precipitation and river run-off establish a low salinity surface layer, causing a permanent salinity stratification in the fjord. Only in the

surface water oxygen and CO₂ are exchanged with the atmosphere, but in the denser bottom water oxygen is absent (anoxic) and the hydrogen sulphide concentration is

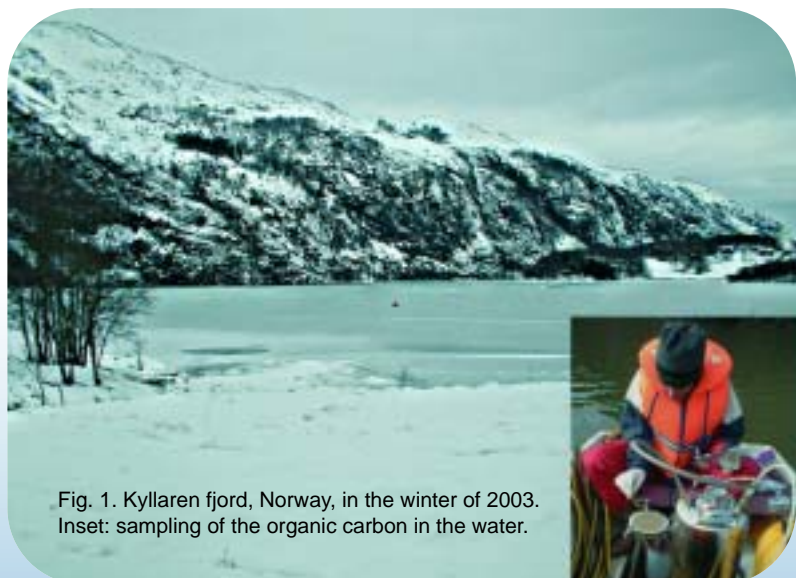


Fig. 1. Kyllaren fjord, Norway, in the winter of 2003. Inset: sampling of the organic carbon in the water.

*Corresponding author: damste@nioz.nl

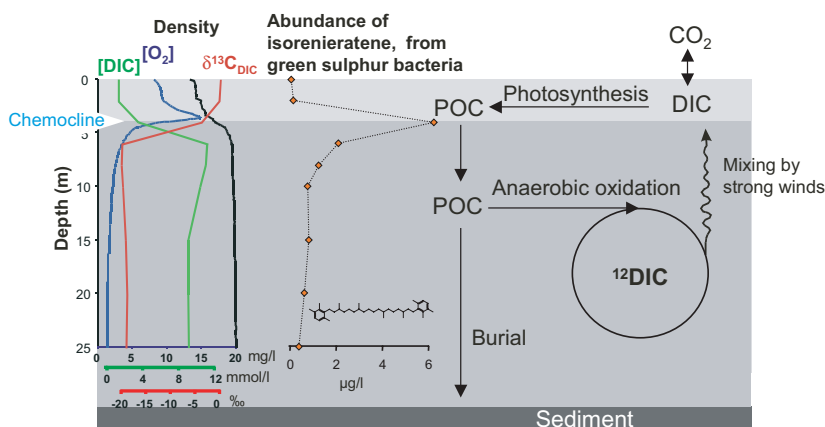


Fig. 2. Increasing DIC concentrations with a concurrent decrease of its ^{13}C content ($\delta^{13}\text{C}$) indicates the accumulation of 'second-hand' DIC derived from remineralization of cellular material (POC) in the bottom water layer of the Kyllaren fjord, as depicted in the model on the right. Isorenieratene is a carotenoid compound only found in green sulphur bacteria living near the chemocline in anoxic water.

fixation. The key enzyme of this biochemical pathway, pyruvate synthase, has a much lower discrimination against ^{13}C compared to the enzyme used by most algae (Rubisco). Indeed, the biological carbon isotope fractionation by GSB of isorenieratene, ϵ_p versus CO_2 , displays an annual average of 4 ‰ in the Kyllaren fjord, and is independent of CO_2 concentration and growth rate of the GSB. Thus, the ^{13}C -depleted isorenieratene

high (Fig. 2). The interface between these two layers is referred to as the 'chemocline'.

Unlike the upper water layer, a high concentration of substantially ^{13}C -depleted dissolved inorganic carbon (DIC) of ca. -19 ‰ was observed below the chemocline in the Kyllaren fjord, throughout the year. This indicates a notable accumulation of 'second-hand' DIC derived from mineralized organic matter (respired DIC). Just below the chemocline, high abundances of the compound isorenieratene were detected. This is a biomarker for the occurrence of photosynthetic green sulphur bacteria (GSB). These organisms flourish when sunlight penetrates to anoxic waters containing hydrogen sulphide (H_2S). GSB use the reductive tricarboxylic acid cycle for CO_2

What is $\delta^{13}\text{C}$?

Stable carbon exists in two atomic forms with masses 12 (^{12}C ; 99 %) and 13 (^{13}C ; only 1 %). Autotrophic organisms, which use dissolved inorganic carbon (DIC) as their primary carbon source, prefer the light ^{12}C form for uptake in their cells. As a result, the ^{13}C form of carbon is depleted in the cell material of algae and autotrophic bacteria compared to DIC in the water column. The average degree of this ^{13}C -depletion is about 25×10^{-3} . (The notation $\delta^{13}\text{C}$ (pronounce delta 13C) against a standard of Vienna Pee Dee Belemnite (VPDB) is in parts per thousand, e.g. $\delta^{13}\text{C}_{\text{organic carbon}} \sim -25$ ‰). The ^{13}C -depletion in the cell material is expressed as the biological carbon isotope fractionation, ϵ_p versus CO_2 .

In formula:

$$\delta^{13}\text{C} = \left(\left(\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}} \right) - 1 \right) \times 1000 \text{ (‰)}$$

the $\delta^{13}\text{C}_{\text{VPDB}} = 0$ ‰ by definition.

The CO_2 in the present-day oceans is in equilibrium with CO_2 level in the atmosphere and consequently $\delta^{13}\text{C}_{\text{DIC}} \sim 0$ ‰.

(-25 to -32 ‰) in the Kyllaren fjord gives evidence of assimilation of the respired CO₂ by photosynthetic GSB.

Fossil isorenieratene was also detected in sediments deposited in ancient oceans during the Toarcian OAE, indicating anoxia in the photic zone. The constant ϵ_p of isorenieratene in the Kyllaren fjord

was subsequently used in the reconstruction of $\delta^{13}\text{C}$ of CO₂ at the chemocline in the Toarcian time. These reconstructions indicate that $\delta^{13}\text{C}$ of CO₂ at the chemocline was indeed influenced by CO₂ that is derived from remineralized organic matter. This could explain the ¹³C-depletion of sedimentary organic carbon

deposited during the OAE compared to the organic carbon deposited before the event, when the Toarcian ocean was oxygenated. Thus our study has shown that recycling of respired CO₂ is an important process in the carbon-cycle of a stratified (shallow) ocean.