Ramped pyrolysis-oxidation-$^{14}CO_2$: A versatile method to elucidate organic carbon reactivity in sediments

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Introduction

Ramped Pyrolysis Oxidation (RPO) is a versatile method that **separates OM fractions based on** their **thermochemical stability.**

Project Aims

1) Establish RPO system optimized for operation with self-constructed trap system & ^{14}C analysis of gas samples with AWI's MICADAS

2) Apply RPO method in two individual studies focussing on Southern Ocean sediment stratigraphy and organic carbon cycling

Advantages of new system vs. Other Systems

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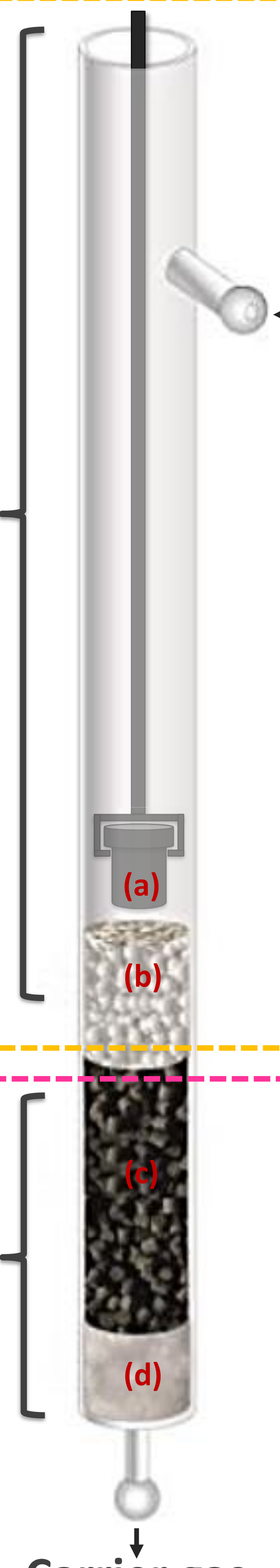
+ **Time efficient**: ~4h: (2 runs, ^{14}C analysis as gas)		- Time intensive: >14h (2 runs, re-combustion, graphitization, ^{14}C analysis)
+ **Blank reduction**: gas tight system & minimum # of preparation steps		- Multiple blank sources: pre-treatment, leaks, re-combustion, graphitization, AMS measurement
+ Technical guarantee & **maintenance support**		- Self conducted maintenance & repairs
+ **Large sample** size: ≤ 3g		- Small sample size: ≤ 400 mg
+ Calibration of **T reading inside crucible**		- Varying positioning of thermocouple → imprecise T control in reactor
+ **Digital control** of trapping; continuous automated record of T, time and CO_2		- Analog reading of T at random times

Technical Setup

1: Pyrolysis

Dynamically heated pyrolysis furnace:

- Sample is placed in crucible (a), lowered into reactor with sample holder & heated without O_2
- Corundum balls (b) create physical barrier to oxidizer
- Gaseous pyrolysis products move downwards in gas stream

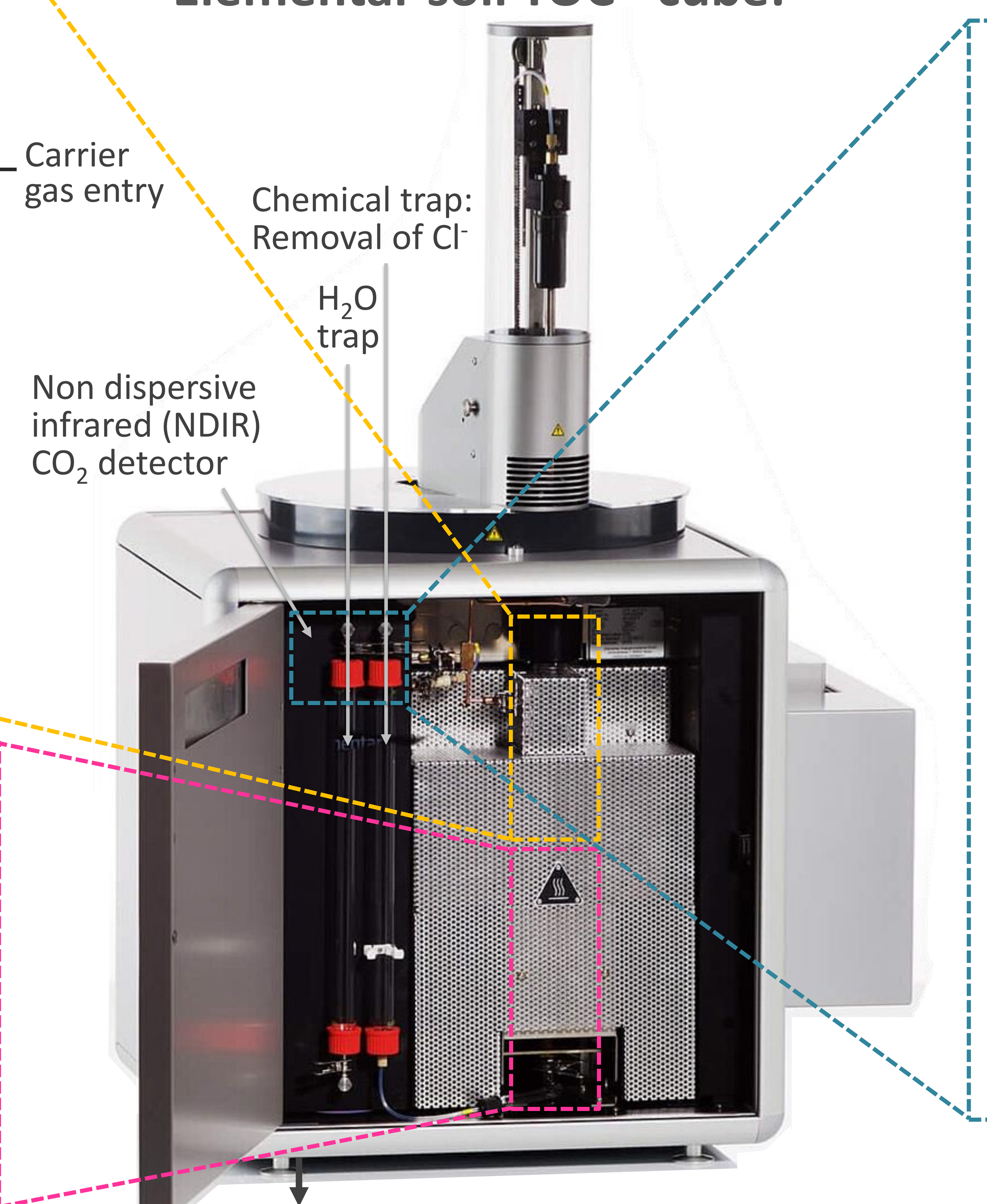


2: Oxidation

Constantly heated oxidation furnace:

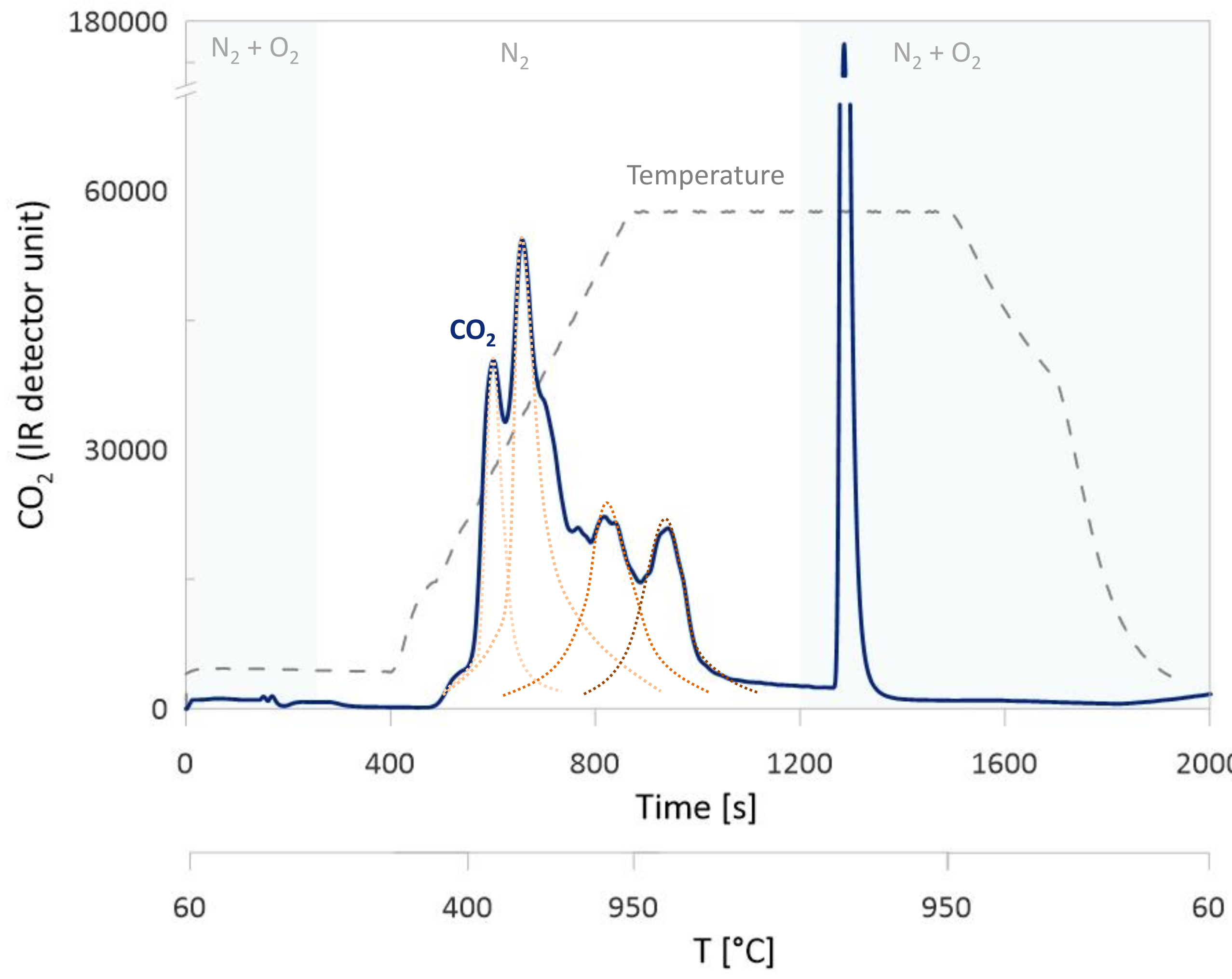
- Mix (c) of CuO (oxidizer) & Pt/Ni (catalyst)
- Pyrolysis products + O_2→ CO_2
- Gas stream is filtered through glass wool (d)

Elementar soli TOC® cube:



3: CO_2 Quantification

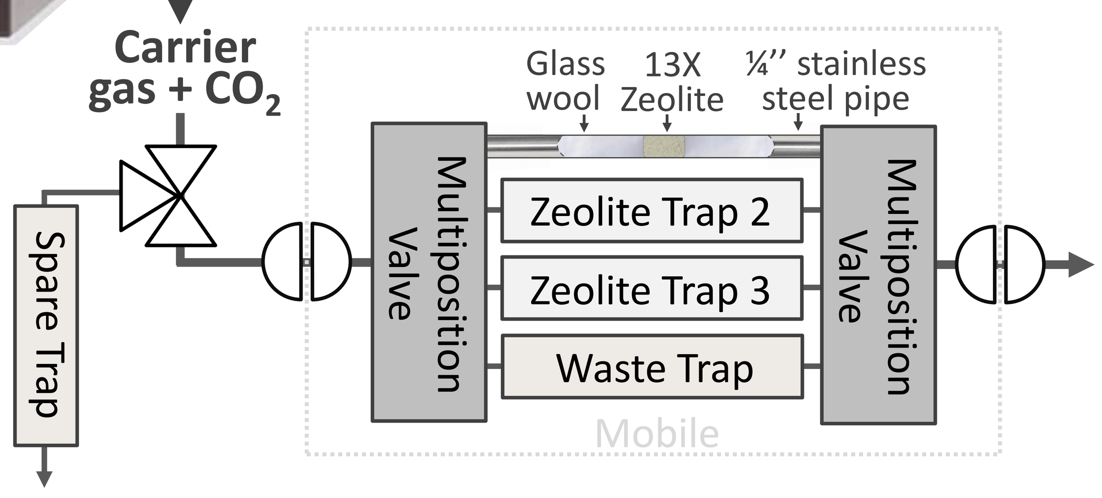
- Online measurement & output of CO_2 concentration



Thermogram of a measurement of decarbonated Antarctic sediment. From 0-250 and 1200-2000 s time, O_2 & N_2 is used as carrier gas (oxidation). Between 250 and 1200 s only N_2 is used (pyrolysis). OM fractions with distinct characteristics decompose at different temperatures, leading to the formation of the four, sub-peaks visible (dashed orange shaded peaks). The large CO_2 peak at 1300 s is created when non-pyrolyzable components are combusted with O_2.

4: Trapping

- Gas stream from soliTOC flows over zeolite trap in trap/valve system & CO_2 adsorbs
- To trap new fraction: multiposition valve is actuated → gas stream flows over next zeolite trap



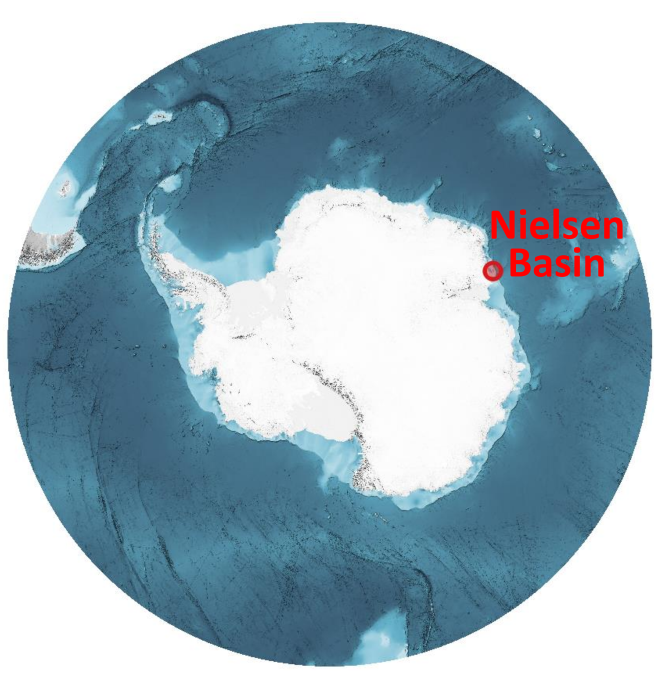
5: Measurement

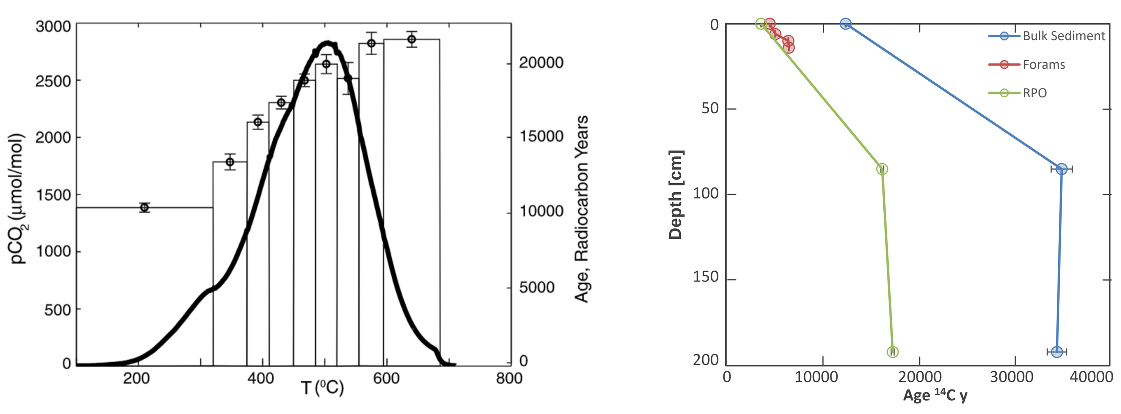
- Entire trap/valve unit is detached from soliTOC & attached to MICADAS
- Each trap is heated to ~400°C → trapped CO_2 desorbs & is transferred into MICADAS
- Each fraction is measured individually

Application studies

1 East Antarctica: Improve Sediment Chronology

- **Aim:** Provide sediment chronology & reconstruct ice sheet retreat by dating OM



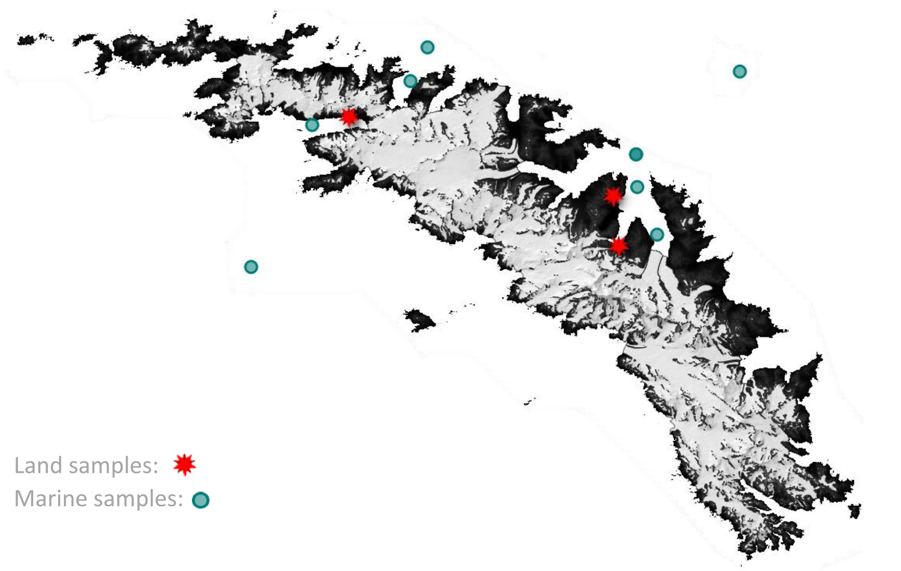


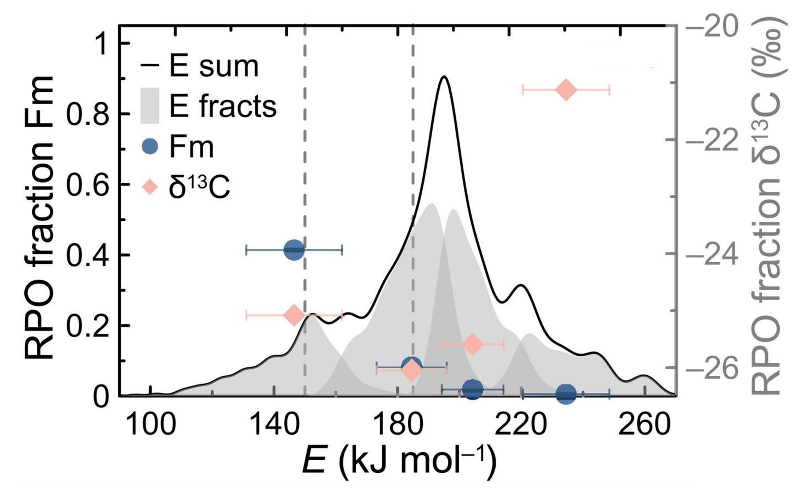
Exemplary RPO results. Left: Thermogram of an Antarctic sediment sample and the individually trapped fractions (boxes) with their respective ^{14}C age (Figure: Rosenheim et al., 2008). Right: Comparison of age models for an Antarctic sediment based on foraminifera, bulk sediment and RPO ^{14}C analyses (data: Subt et al. 2017).

Distinct OM fractions are separated, trapped & ^{14}C analysed. The age is determined for a thermochemically labile & young fraction of marine OM associated with transition towards seasonally open marine conditions during ice sheet retreat.

2 South Georgia Island: OC preservation & reactivity

- **Aim:** Characterize reactivity of OM released from retreating glaciers & permafrost





Exemplary RPO results: Activation energy distribution *p(E)*, $\delta^{13}C$ values and Fm values for 4 RPO fractions (grey-shaded areas) from a sediment sample from Yakutat Bay fjord. Figure: Cui et al. (2022)

Inverse modelling is applied to derive the energy required to break chemical bonds within organic molecules and between OM & minerals. Findings are correlated to ^{14}C signature of individual fractions to characterize their reactivity and possible preservation potential.

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