Thermal Maturation Effects on the Nitrogen Isotopes in Marine Shales: A Case Study of the Woodford Shale*

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Abstract

In this study, we examine the use of sedimentary δ15N as a proxy for water column redox state during the deposition of productive marine shales. On geologic time scales, the most influential reactions in the nitrogen cycle are nitrogen fixation, nitrification, and denitirification, and their relative predominance is controlled by the redox state of the water column. Associated with each of these reactions is a characteristic nitrogen isotopic fractionation, which is reflected in the organic matter produced; this organic matter is subsequently transferred into the sediments. Both nitrogen fixation and nitrification have relatively low fractionation factors that result in depleted δ15N values for organic matter. Denitrification prefers to utilize the isotopically lighter 14N nitrate, therefore enriching the residual nitrate pool, which is then used to produce organic matter with enriched δ15N values. Incomplete denitrification is predominant under suboxic water column conditions, while nitrogen fixation and/or nitrification are dominant in anoxic and oxic environments. Therefore, bulk sediment samples with enriched δ15N values can be assumed to have been deposited under suboxic conditions, while intervals with depleted δ15N values would likely have been deposited under anoxic or oxic conditions, provided that post-depositional diagenesis does not occur.

In order to evaluate the use of sedimentary δ15N as a proxy for water column redox states, we compared the δ15N values from the anoxic Woodford Shale with those from the suboxic Springer Shale. Four cores were chosen in Grady and Custer counties in Oklahoma based on location within the Anadarko Basin and the relative locations of the Woodford and Springer cored intervals. In general, we found that anoxic depositional environments have relatively low sedimentary δ15N values, while relatively enriched sedimentary δ15N values correlate to suboxic depositional environments. These results confirm that sedimentary δ15N can be used as a tool to identify and evaluate anoxic intervals, which can enhance the identification of productive intervals within shales.

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May 20, 2013

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Outline

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- Introduction
- Background
- Study Area
- Results
- Discussion/Conclusions

Goal: To identify the effects of thermal maturation on the nitrogen isotope signal of the Woodford Shale.

Introduction: *Redox States*

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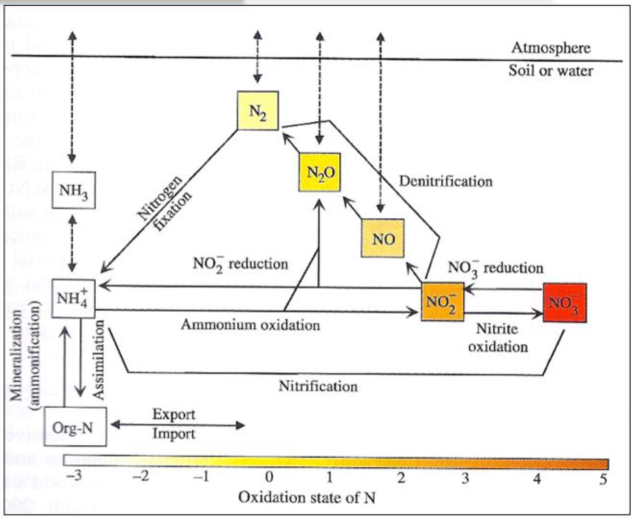
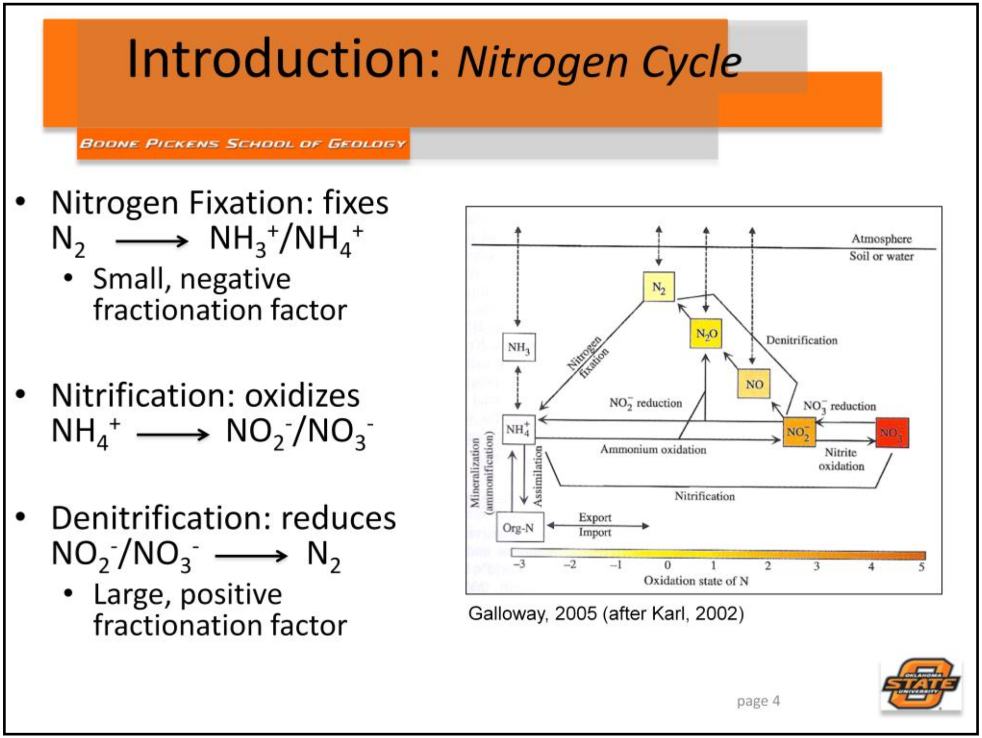


Galloway, 2005 (after Karl, 2002)

Presenter's notes:

- This is a schematic of the nitrogen isotopes showing the reactions that dictate the cycle
- These cycles are strongly influenced by the redox states of the water column and each have an associated fractionation factor
- The cycle consists of several cycles, but on geological time scale the temporal reactions are masked by three dominant reactions:
  - Nitrogen fixation
  - Nitrification
  - Denitrification



Presenter's notes:

- Fixation:
    - Reduction process of fixing N2 to NH3/NH4 by nitrogen fixing bacteria.
    - N2 has a redox state of 0. When it is fixed, the N receives electrons resulting in a -3 redox shift.
- Nitrification:
    - Oxidation process of converting NH4 to NO2/NO3.
    - NH4 has a redox state of -3 and when it is oxidized, the N loses electrons, resulting in a positive shift to redox states of +3 and +5.
- Denitrification:
    - Reducing process of converting NO2/NO3 back to N2
    - When the nitrates/nitrites are reduced to N2, the lose of oxygen produces a positive charge for the N atom, resulting in a negative shift to a redox state of 0.
- The conversion of nitrogen species in each reactions has a associated fractionation factor (which is an expression of the extent of fractionation)
    - Fixation:
        - Fractionation associated with fixation is relatively small, negative $\delta^{15}N$ values (~ 0.7 ‰, but can range from -2.2 – 3.7‰)
        - Remineralization of the light $\delta^{15}N$ OM resulting from N-fixation and nitrification (with little denitrification) results in relatively small, negative fractionation on the nitrate pool and gets incorporated into the sediments
    - Denitrification:
        - Denitrifiers preferentially utilize the light isotope (^{14}N), which results in a large, positive fractionation factor on the nitrate pool producing enriched nitrate.
        - Enriched nitrate becomes assimilated into microorganism cells and incorporated into sediments when the organisms die off

Introduction: *Nitrogen vs. Oxygen*

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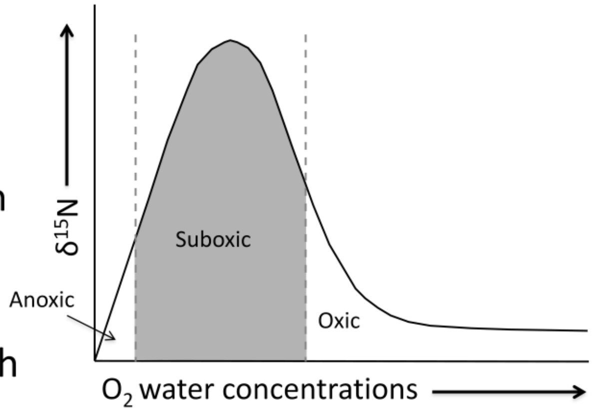
- Evolution of sedimentary $\delta^{15}N$ with increasing O_2
- $\delta^{15}N$ increases with increasing O_2 until critical point
- $\delta^{15}N$ decreases with increasing O_2



Modified from Quan and Falkowski, 2009

Presenter's notes:

- The $\delta^{15}N$ values are strongly related to the oxygen concentrations of the water column
- The graph to the right is a schematic diagram of the effects of oxygen concentrations on the $\delta^{15}N$ values of nitrate.
- As the oxygen concentrations increase, the $\delta^{15}N$ values increase to a critical point (~ 30µM of oxygen), then decreases.
- At a point of low oxygen levels (suboxic environments) the increase of $\delta^{15}N$ values is attributed to denitrification. The presence of oxygen permits the production of nitrate, which is the primary electron donor for the microorganisms.
- At the critical point, oxygen affects the enzyme responsible for the denitrification process, which results in decrease of denitrification.
- The denitrification does not cease, it is just relatively miniscule compared to the nitrate pool.
- As oxygen concentrations continue to rise, you enter the oxic regime and nitrogen fixation reaction becomes dominant.

Introduction

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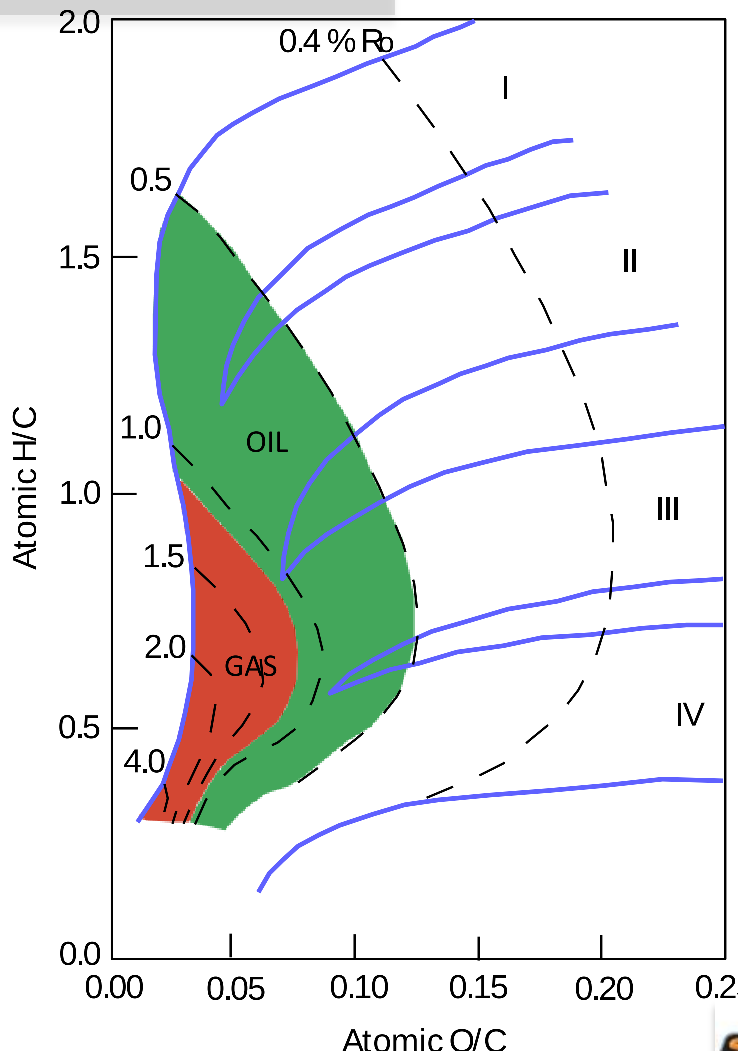
- Setback:
  - Accurate knowledge of the original sedimentary $\delta^{15}N$ values

- Thermal maturation
  - Increase of R_o
  - Decrease in weight % of TN and TOC (Boudou et al., 2008)
  - Enrichment of sedimentary $\delta^{15}N$ and organic $\delta^{13}C$ values (Macko, 1985; Rice et al., 1988)



Modified from Seewald, 2003

Hypothesis

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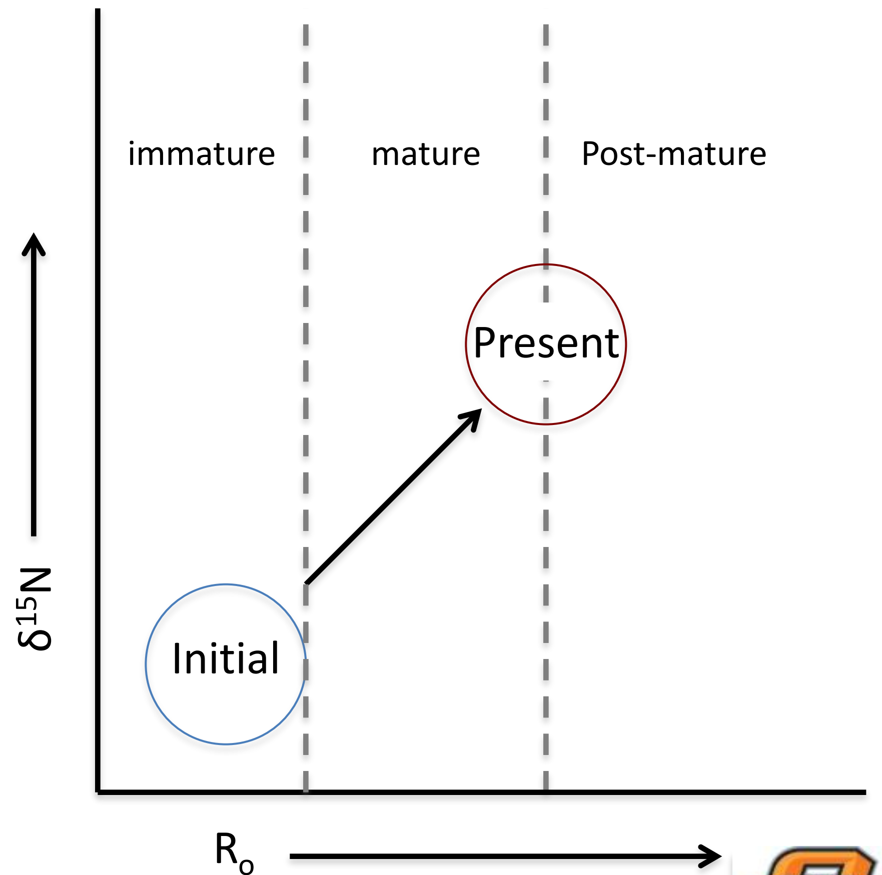
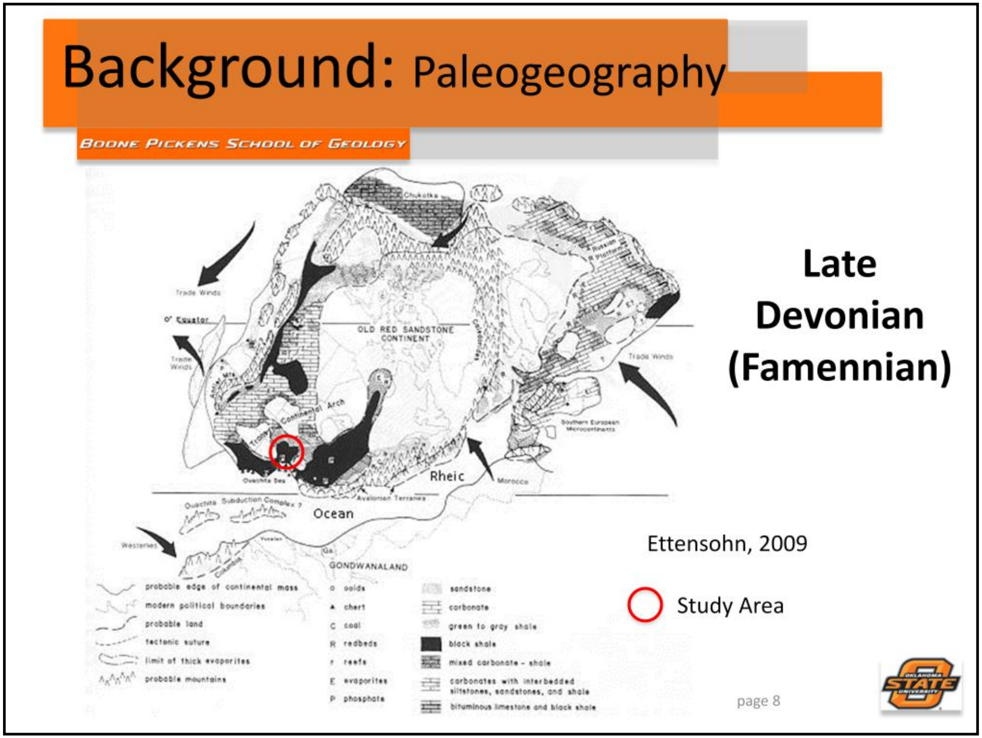
- Hypothesis: Thermal maturity will induce a consistent positive shift of the sedimentary $\delta^{15}N$ values from the original deposited $\delta^{15}N$ values to the final measured $\delta^{15}N$ values.
- Assume: Initial $\delta^{15}N$ values from OM deposited in anoxic conditions; consistent organic matter and constant hydrocarbon production rates





Presenter’s notes:

I) In the late Devoian, an epicontinental sea inundated the continent
    I) Topo highs are the Padernal Uplift (west), the Trancontinental Arch (northwest), and the Ozark Plateau (east)

II) Sediment deposition is believed to be sourced from the east off the Ozark Plateau

Background: Burial History

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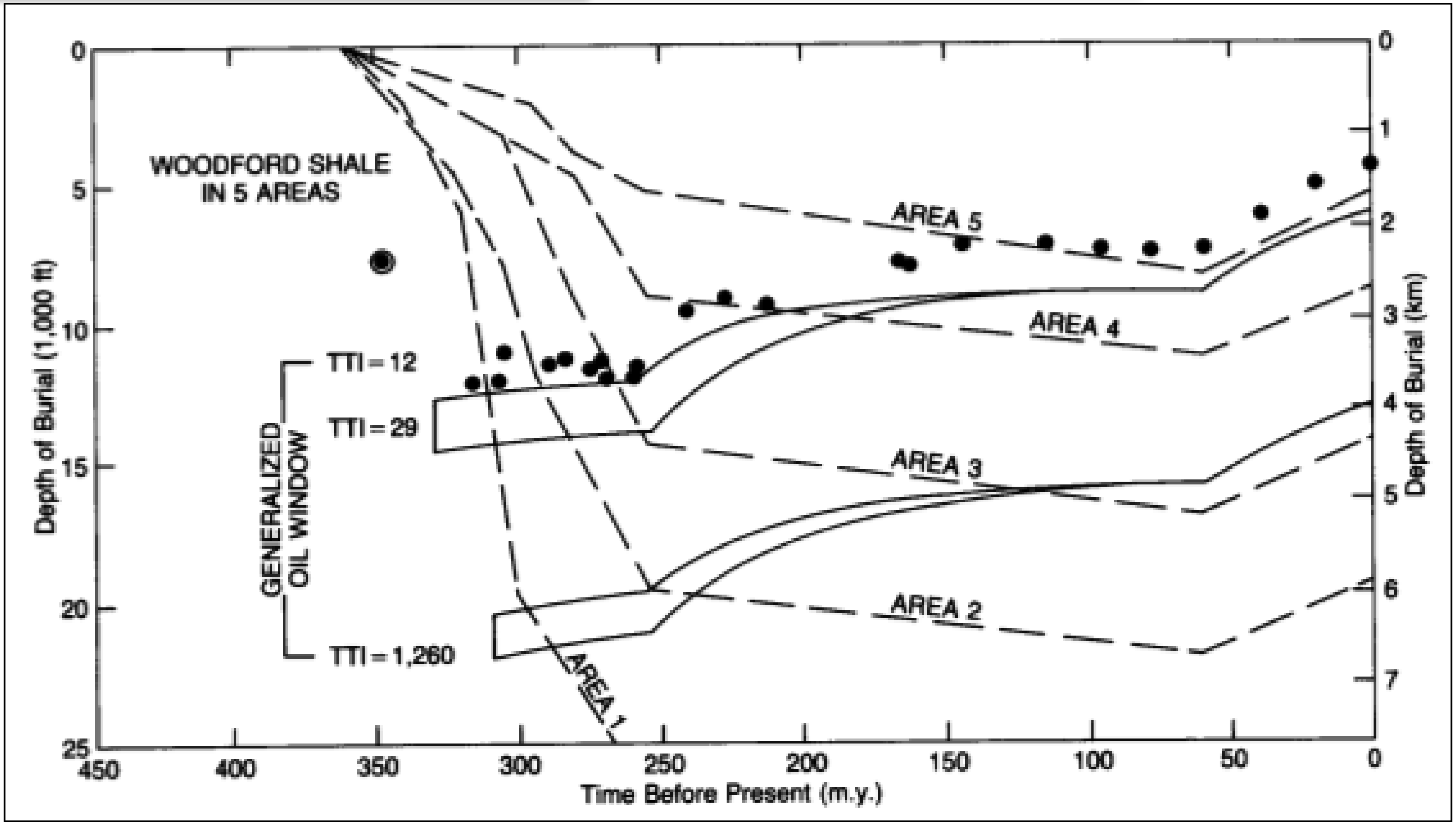

Schmoker, 1989

Study Area

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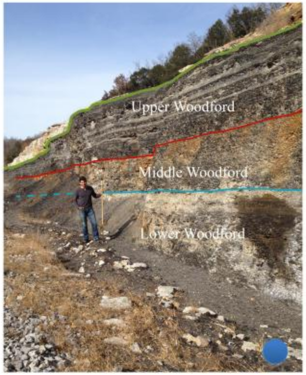

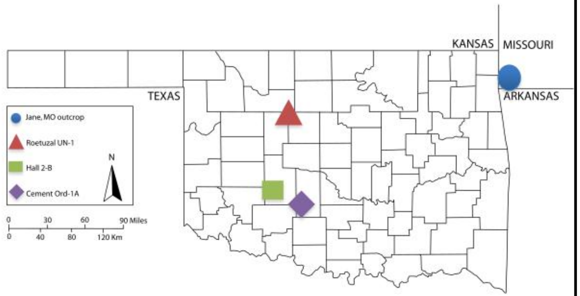

- 1 outcrop location
- Woodford Shale in Jane, MO (JMOC)

- Three core locations
  - Roetzal UN-1 (ROETUN); Kingfisher Co.
  - Hall 2-B (H2B); Caddo Co.
  - Cement Ord-1A (CO1A); Grady Co.

Presenter's notes:

- The study area encompasses a majority of the Anadarko basin, with one area in the Ozark Plateau
- Photo to the left is the outcrop of the Chattanooga shale (Woodford equivalent)
    - Outcrop has all upper, middle, and lower Woodford exposed
- Map to the right shows the sample locations

Methods

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- Samples collections:
  - Core: variable on quality and OPIC guidelines
- Stored in Ziploc bags
- Transported to laboratory for analyses
- Samples collected for Conodont CAI

Presenter's notes:

- Core image of the upper Woodford
  - Sometimes the outcrop was in poor condition where the rock was in several pieces
  - OPIC regulations on sampling: no sampling within a foot of pre-sample location
    - H2B: 6 ft average interval
    - Roetun: 2 ft average interval
    - CO1A: 5 ft average interval
    - JMOC: 3 in interval for the entirety of the outcrop
- Outcrop image of samples collected for conodont cai analysis
  - Sample interval: 1 cm for the upper 1 m of the Woodford

Methods

- Nitrogen and Carbon Isotope Analysis: ThermoFinnigan Delta Plus Isotope Ratio Mass Spectrometer
- Total Nitrogen (TN) and Total Organic Carbon (TOC) Concentrations: Costech Elemental Analyzer
- Thermal Maturity:
  - R_o values from Cardott, 2012
  - Verified by Conodont Color Alteration Index (CAI)

Results: *Thermal Maturity*

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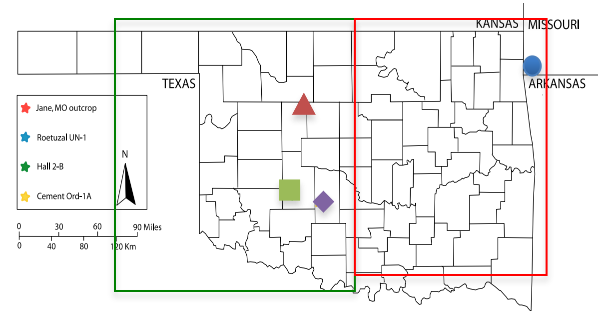
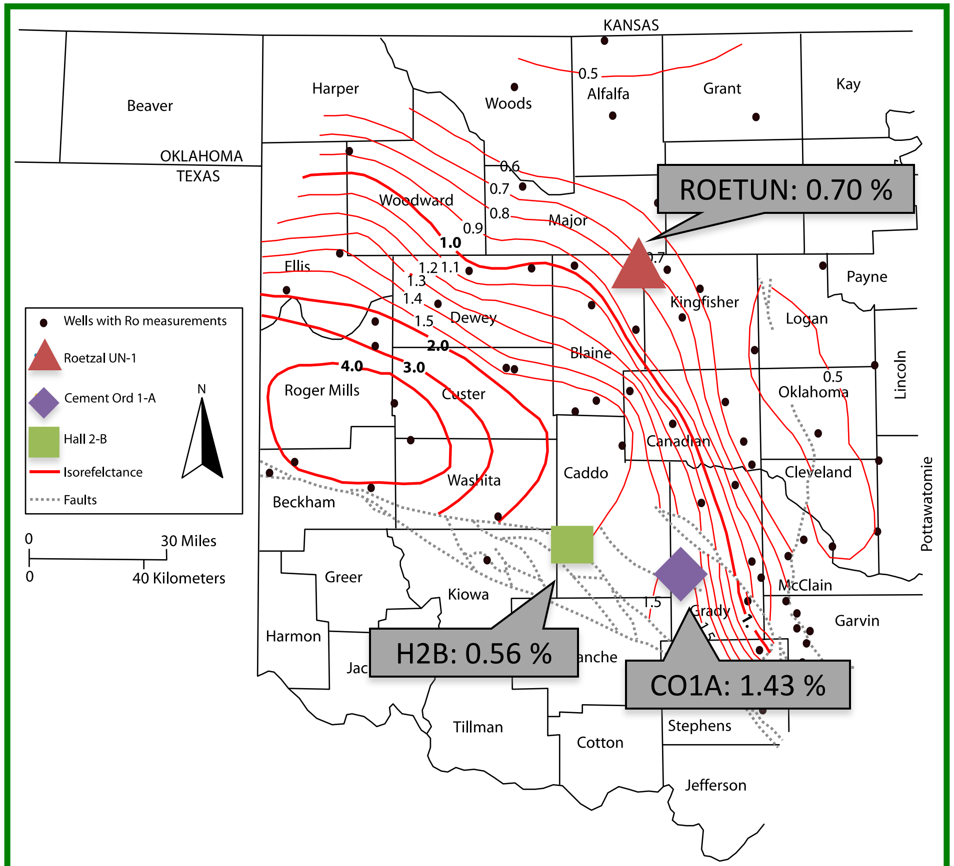
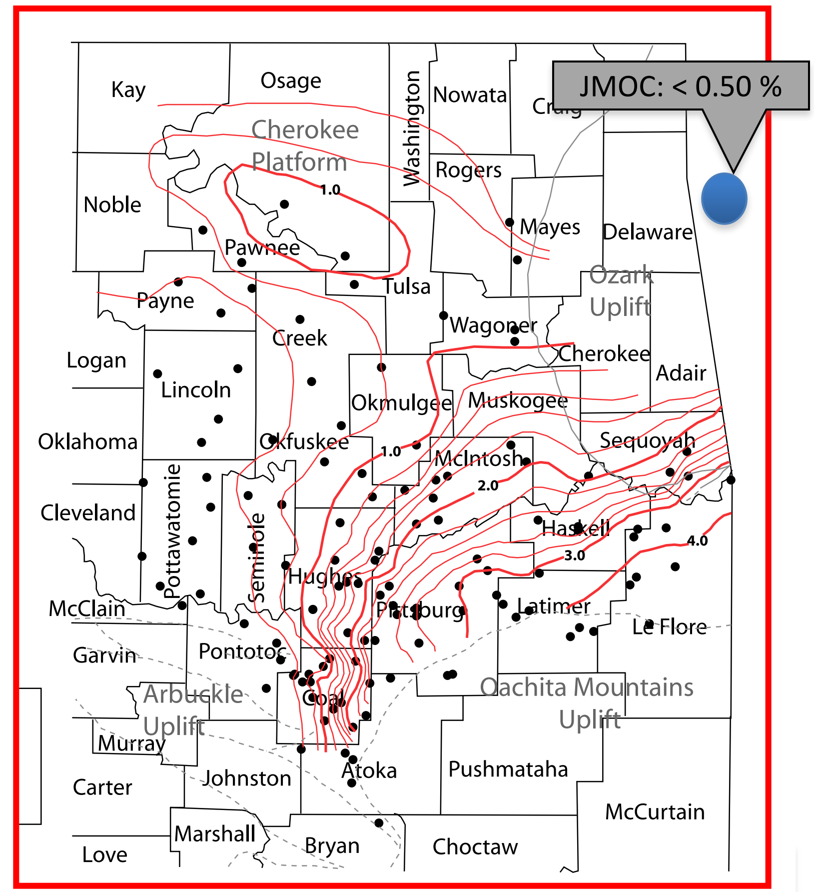


Anadarko Basin



Arkoma Basin



Modified from Cardott, 2012

Discussion: *Evolution of $\delta^{15}N$*

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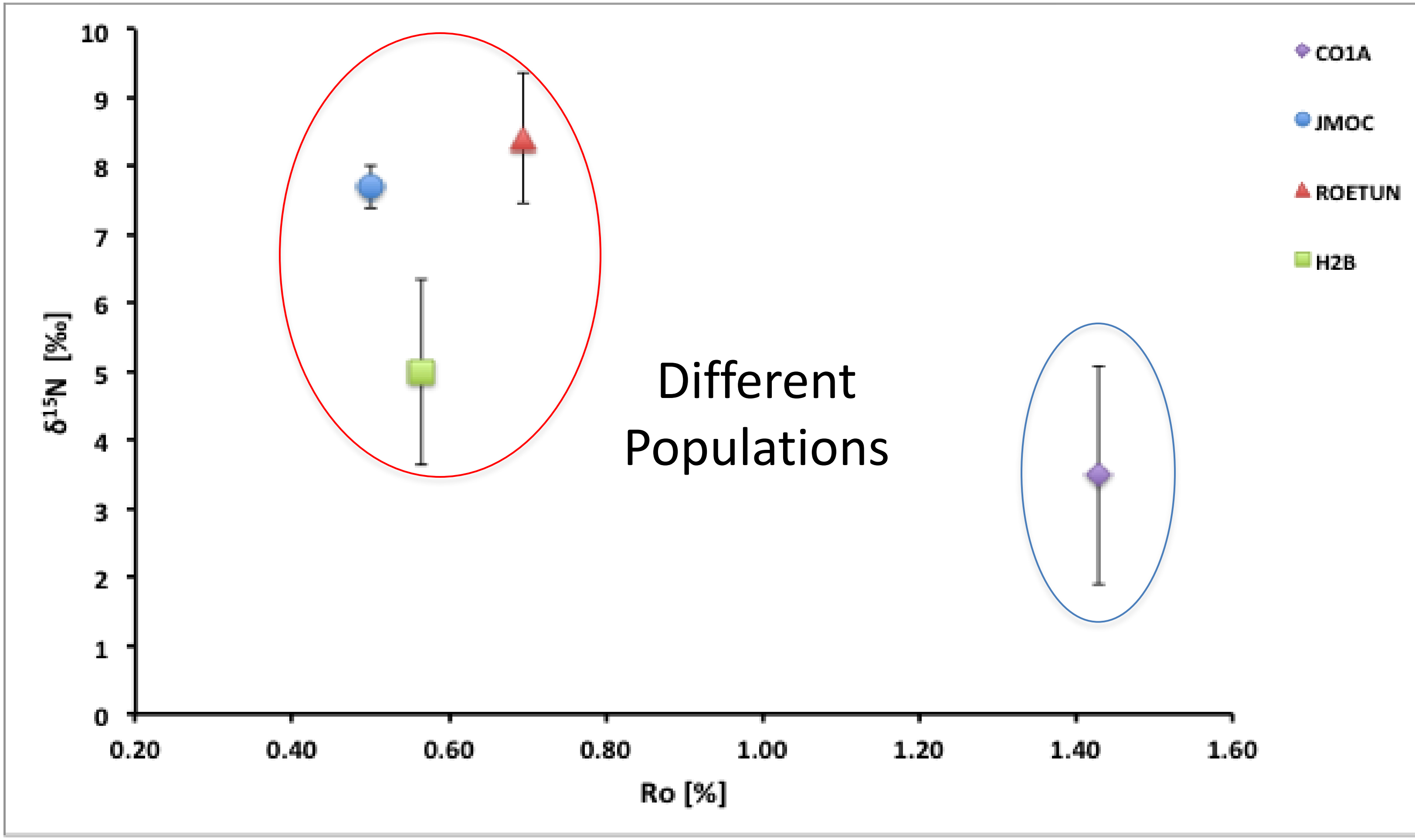
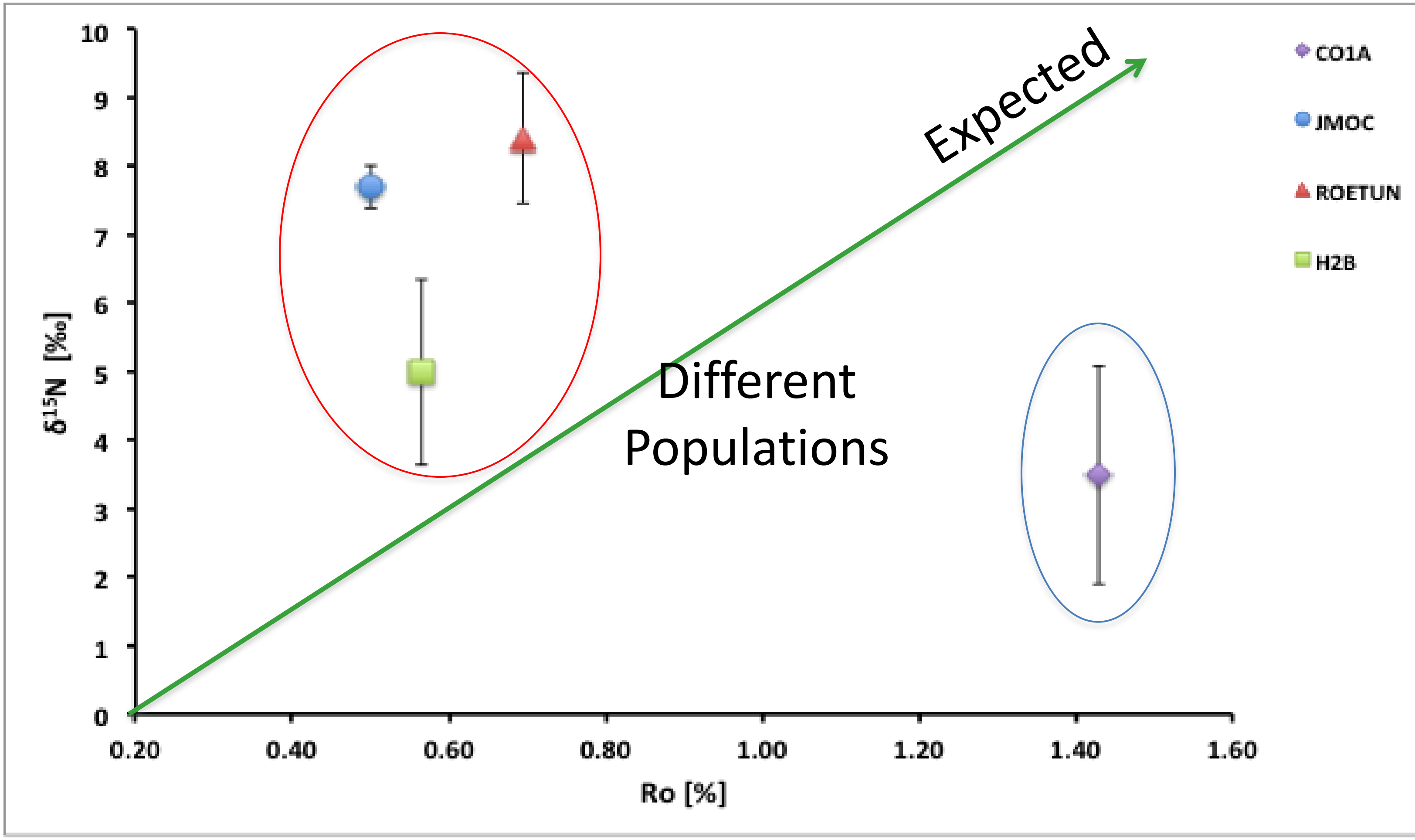


Discussion: *Evolution of $\delta^{15}N$*



Discussion: *Evolution of $\delta^{13}C$*

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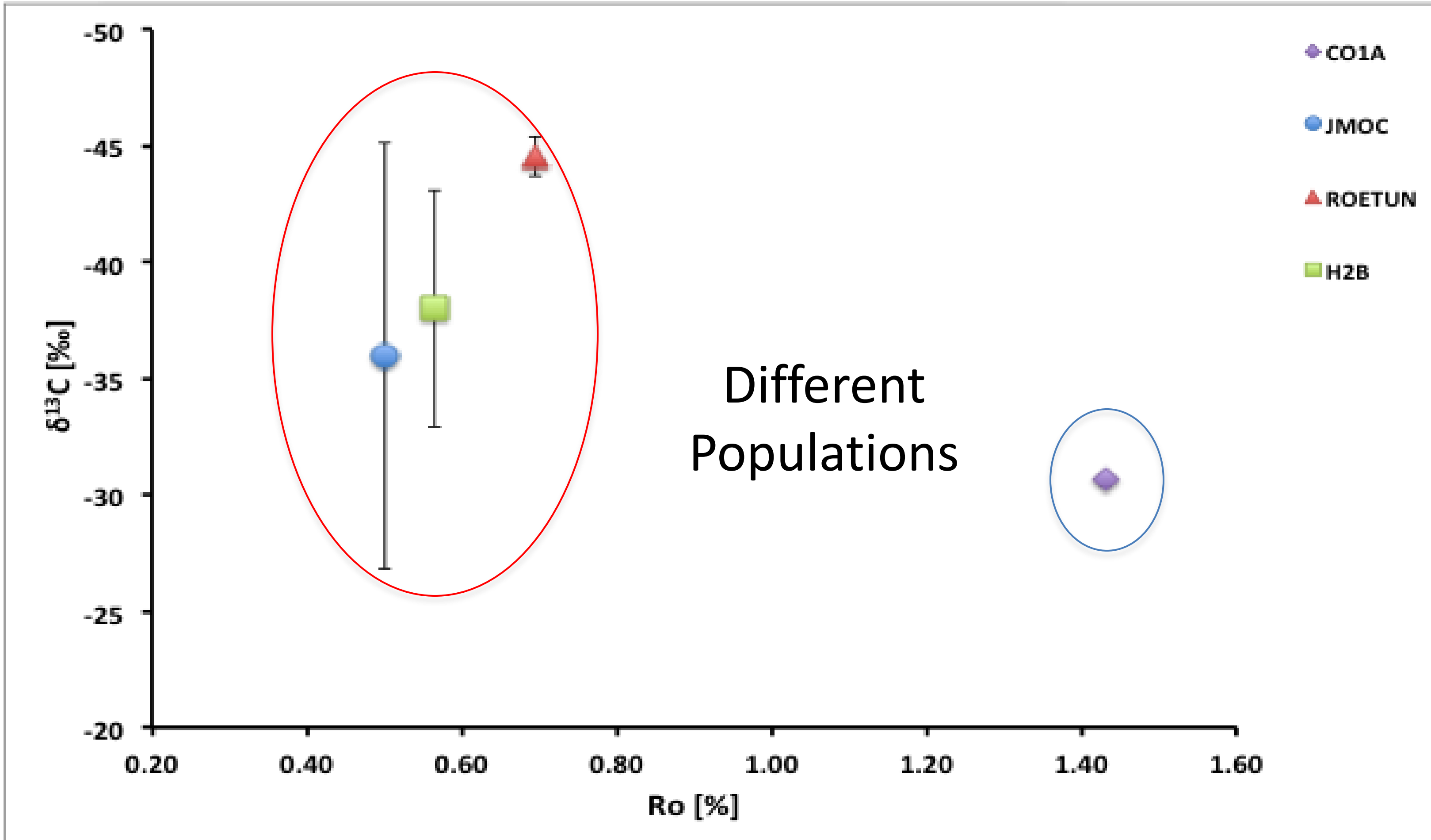

Discussion: *Evolution of $\delta^{13}C$*

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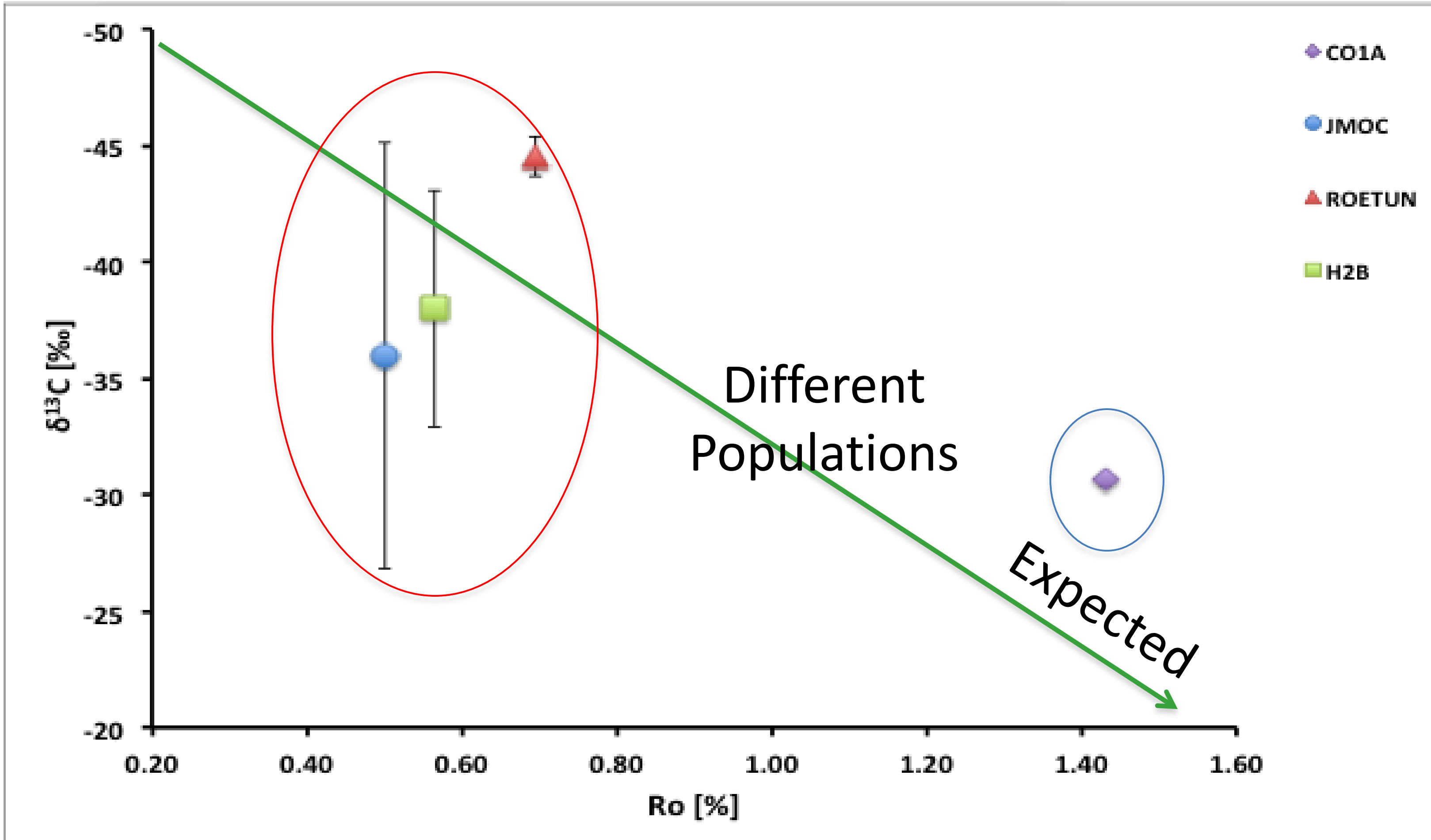

Discussion: *Evolution of TN*

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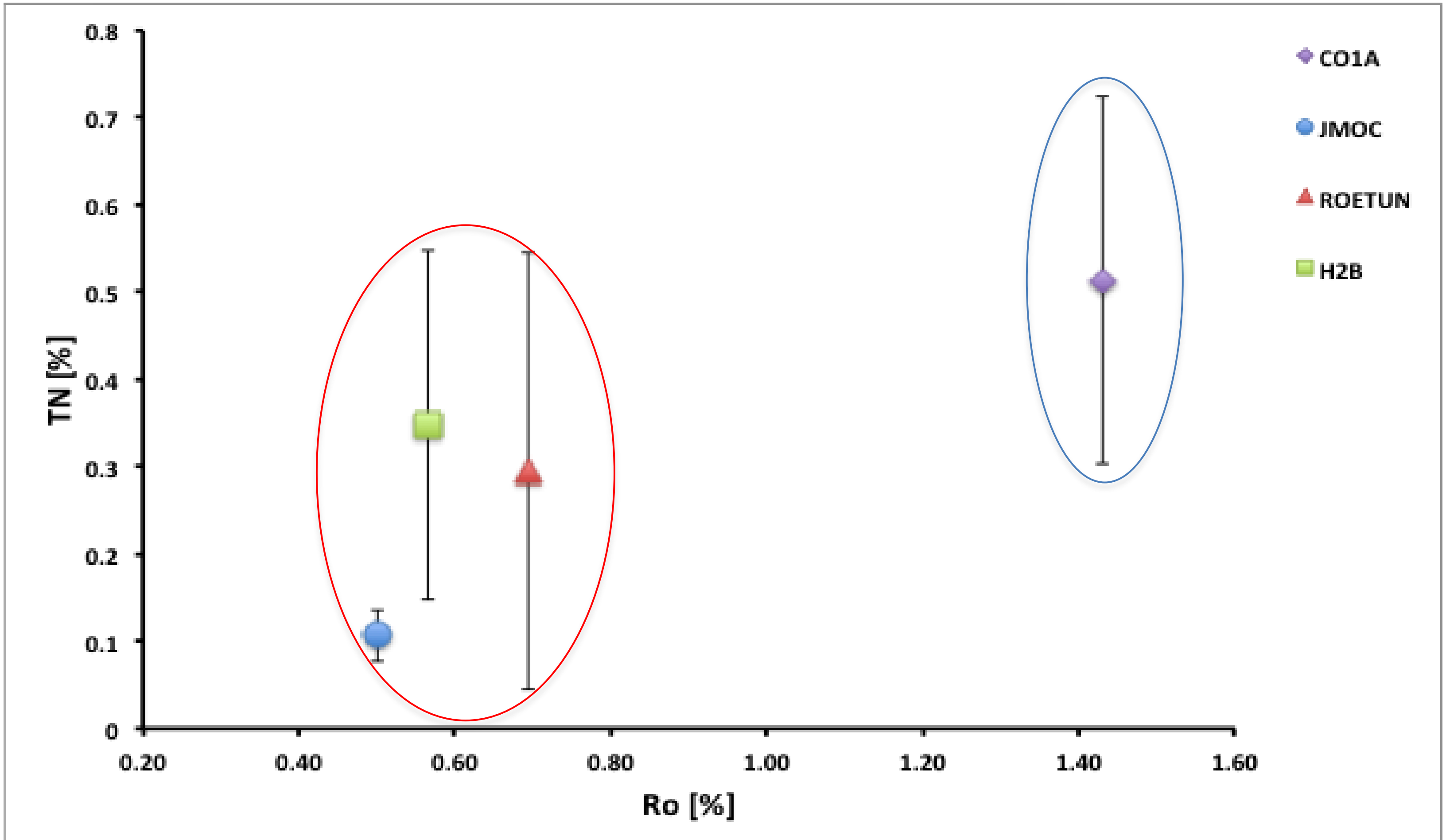

Discussion: *Evolution of TN*

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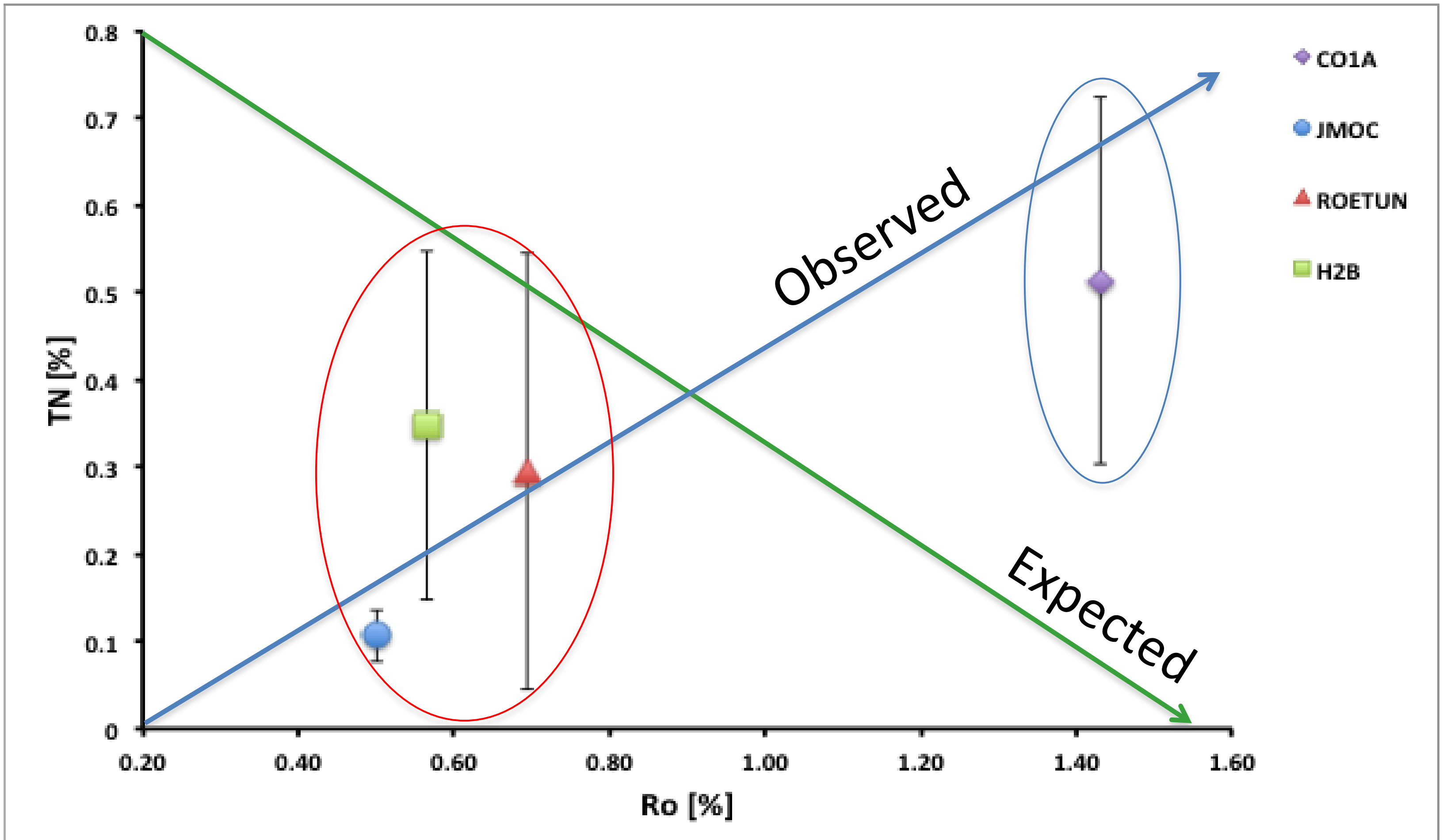
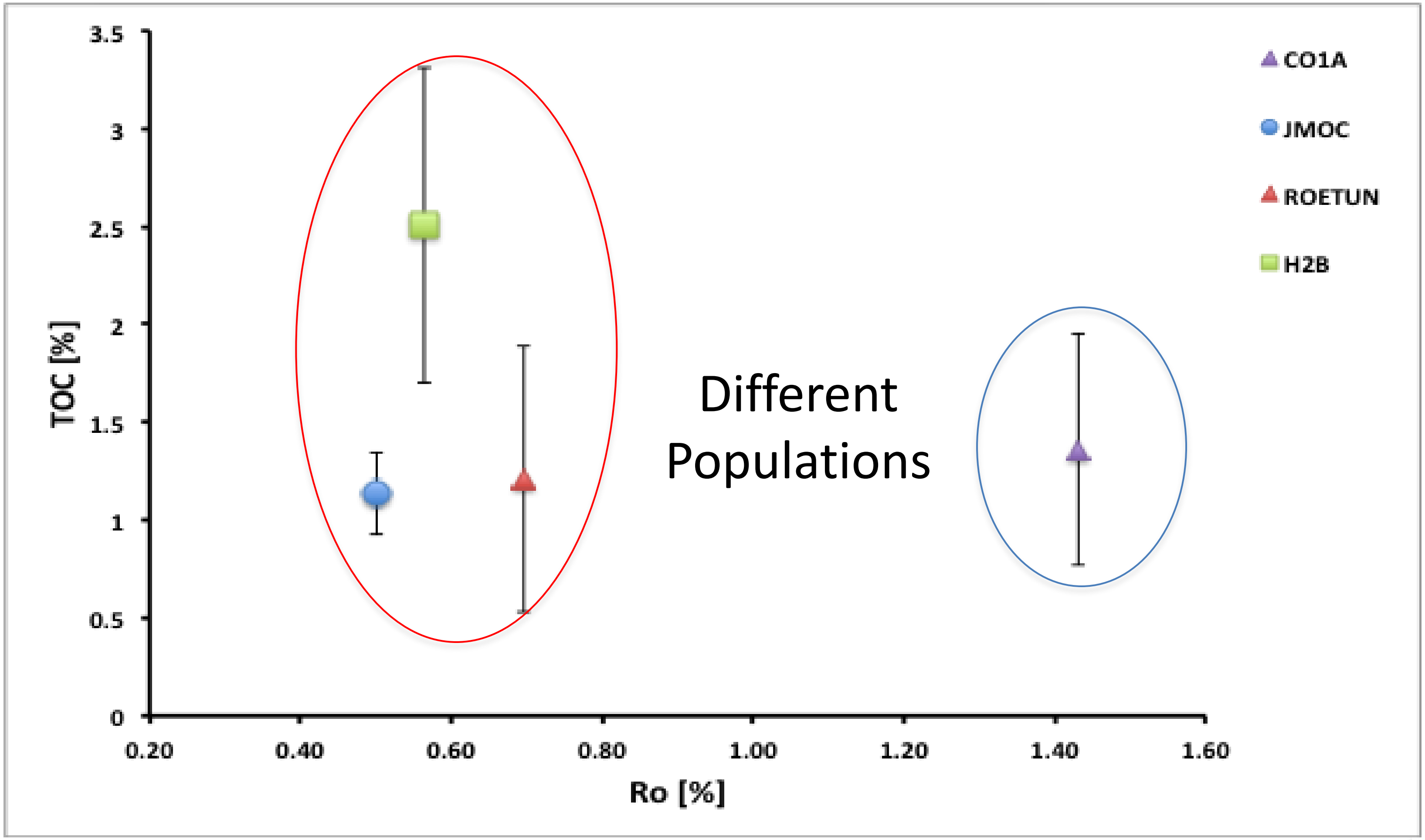


Discussion: *Evolution of TOC*



Discussion: *Evolution of TOC*

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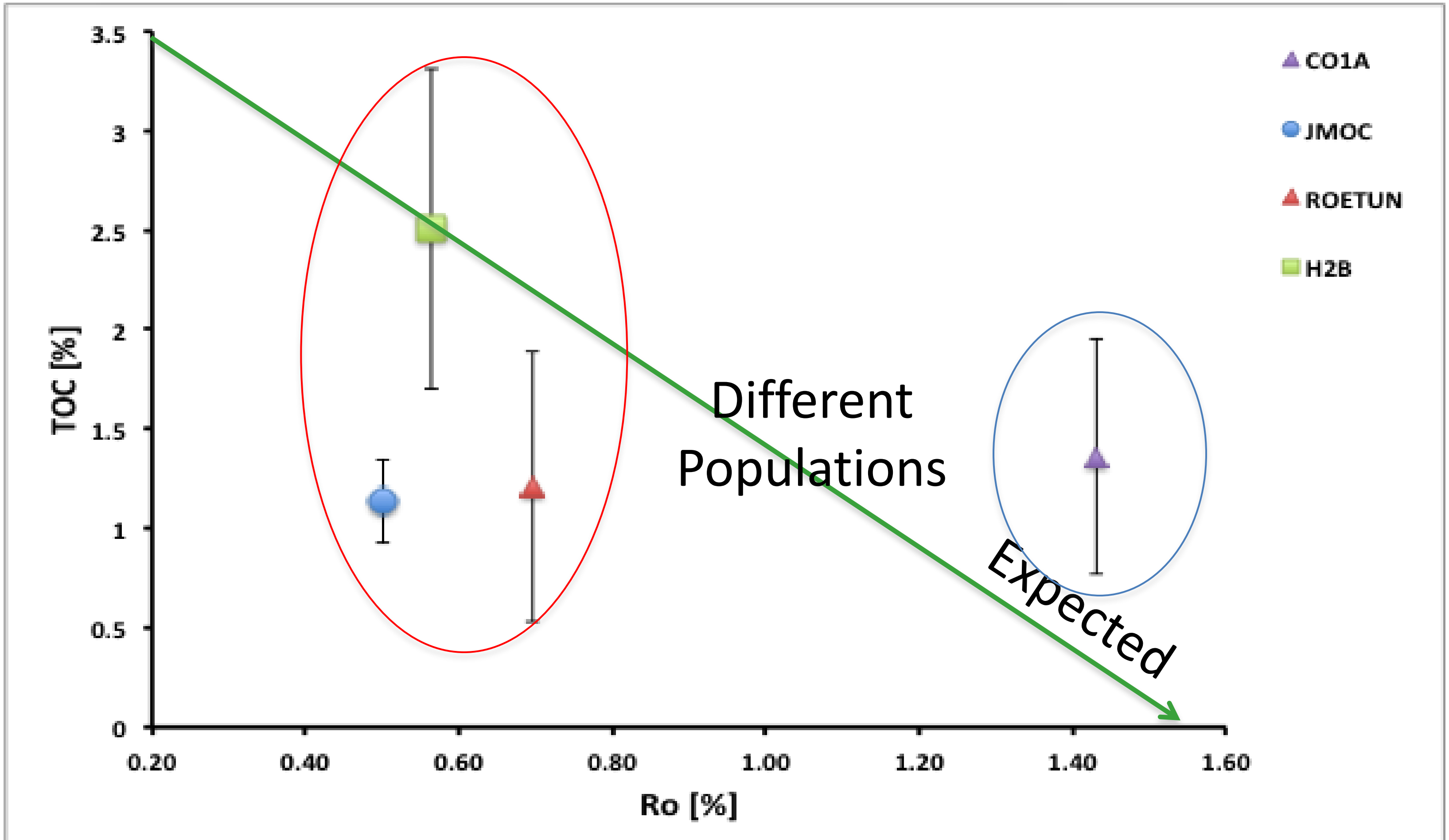

Discussion: *Different depositional settings*

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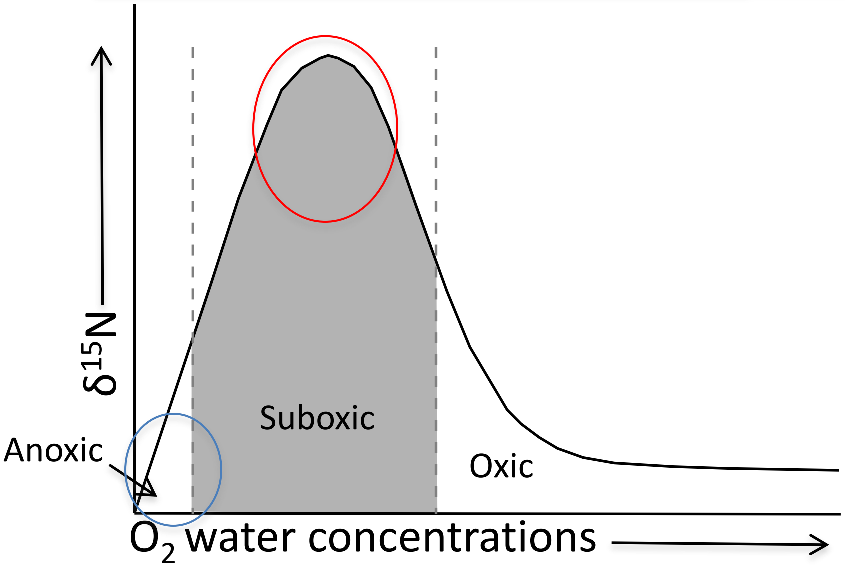

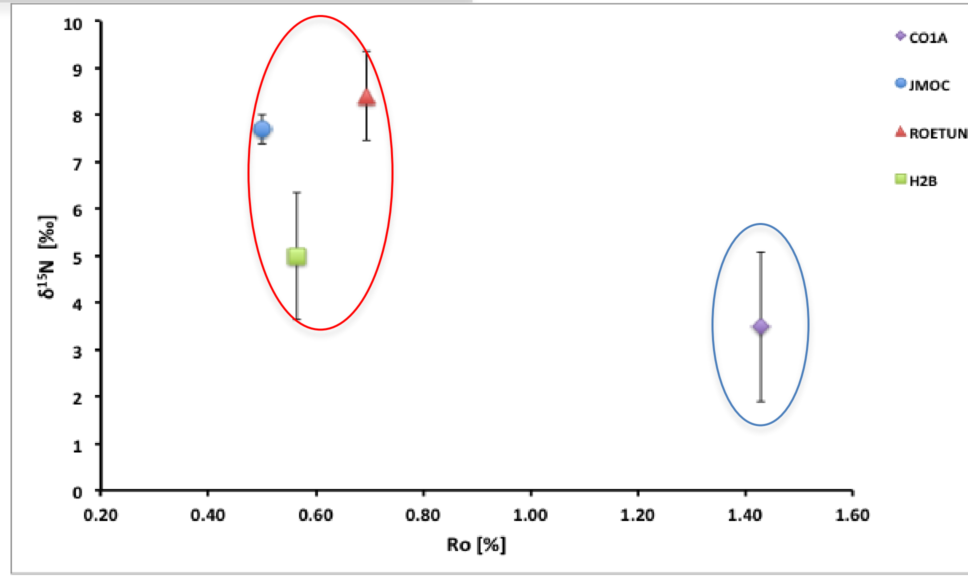

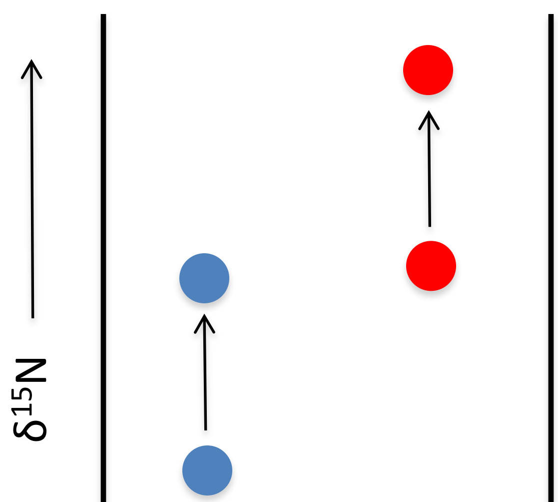

- Two different initial depositional settings
  - Anoxic
  - Suboxic/Hypoxic

Conclusions:

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- The $\delta^{15}N$ data primarily reflects initial redox water column conditions during deposition
- The data does not support our initial hypothesis
- Data suggests different initial depositional environments
  - Suboxic: JMOC, ROETUN, and H2B
  - Anoxic: CO1A
- JMOC, ROETUN, H2B shelf and basin margin
- CO1A located in the basin depocenter

Presenter's notes:

- Given the presented data, the Thermal Enrichment Model does not explain the data.
- Therefore, something is causing the depletion of $\delta^{15}N$ and $\delta^{13}C$ values, as well as the increase in TOC and TN.

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