

QUANTITATIVE AND SPECIFIC RECOVERY OF ORGANIC AND MINERAL SULFUR FOR MULTI-ISOTOPE ANALYSIS

I. Jovovic, V. Grossi, P. Adam, F. Gelin, I. Antheaume, M. Ader & P. Cartigny



INTRODUCTION

BIOGEOCHEMICAL CYCLE OF SULFUR SPECIES

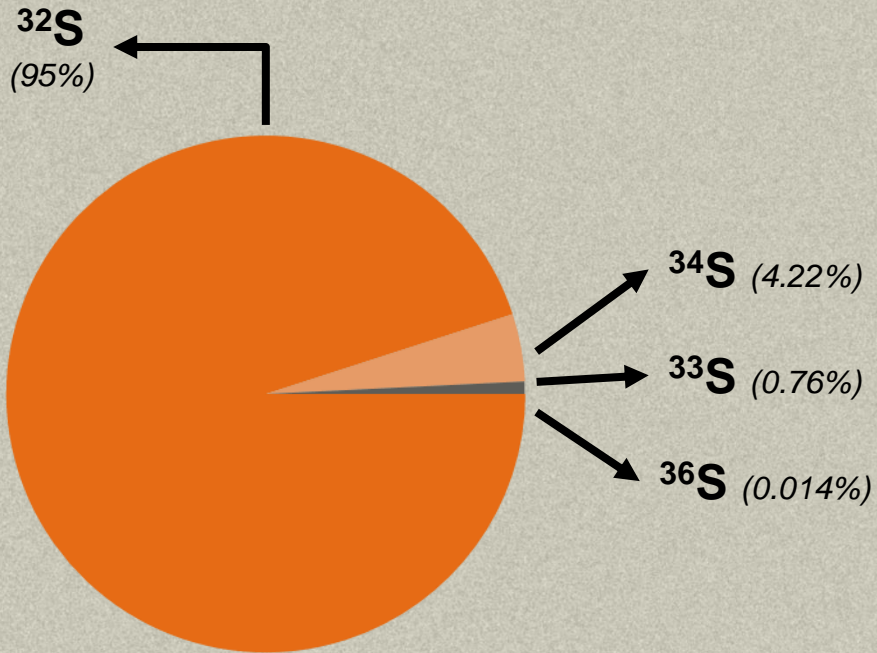
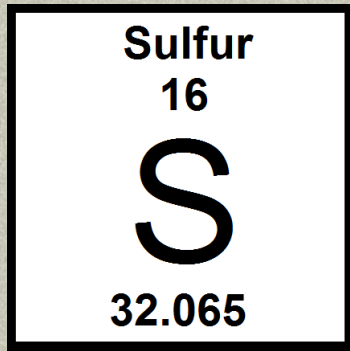


Lake Dziani Dzaha (Mayotte)



Green River Fm (USA)

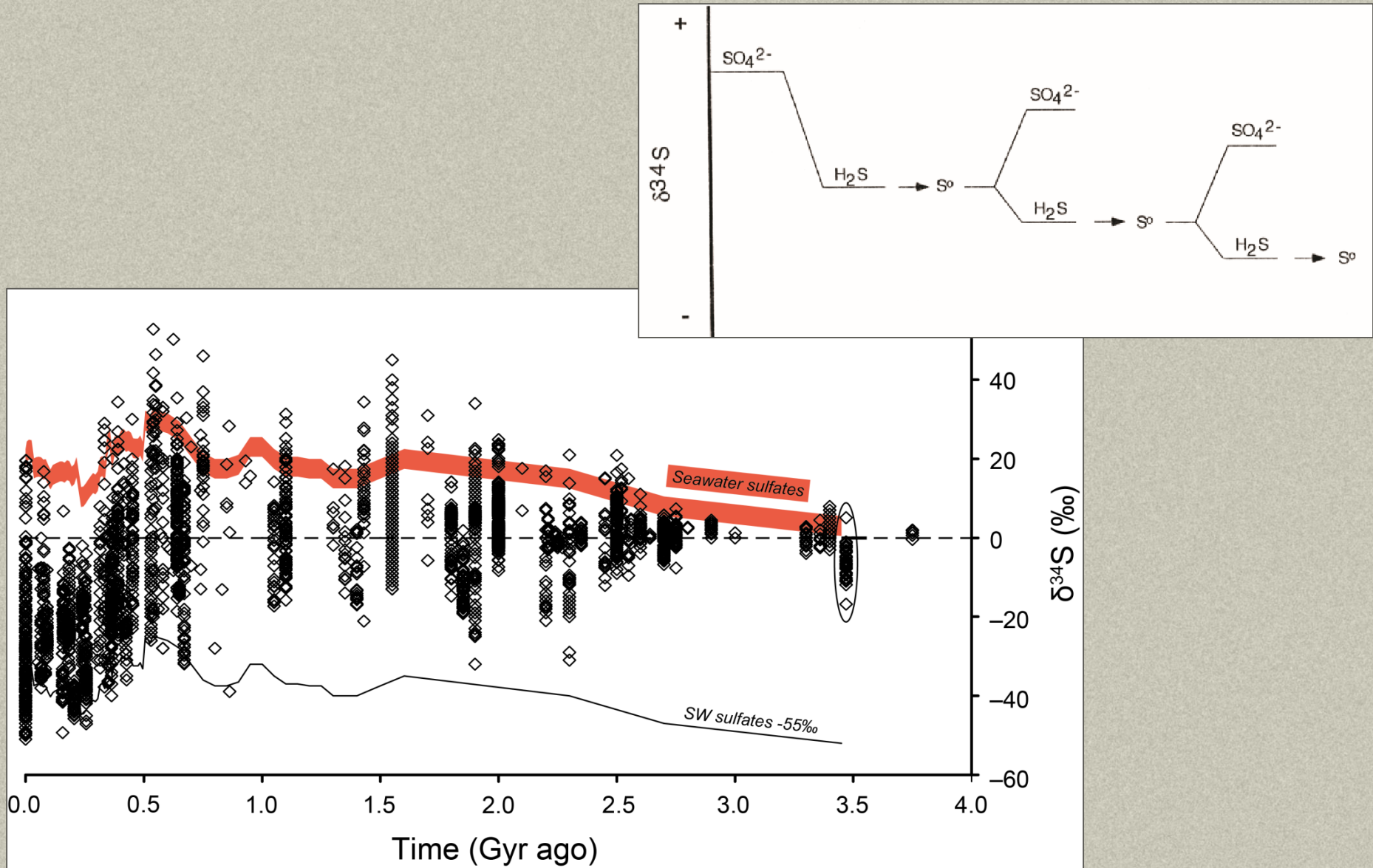
SULFUR STABLE ISOTOPES



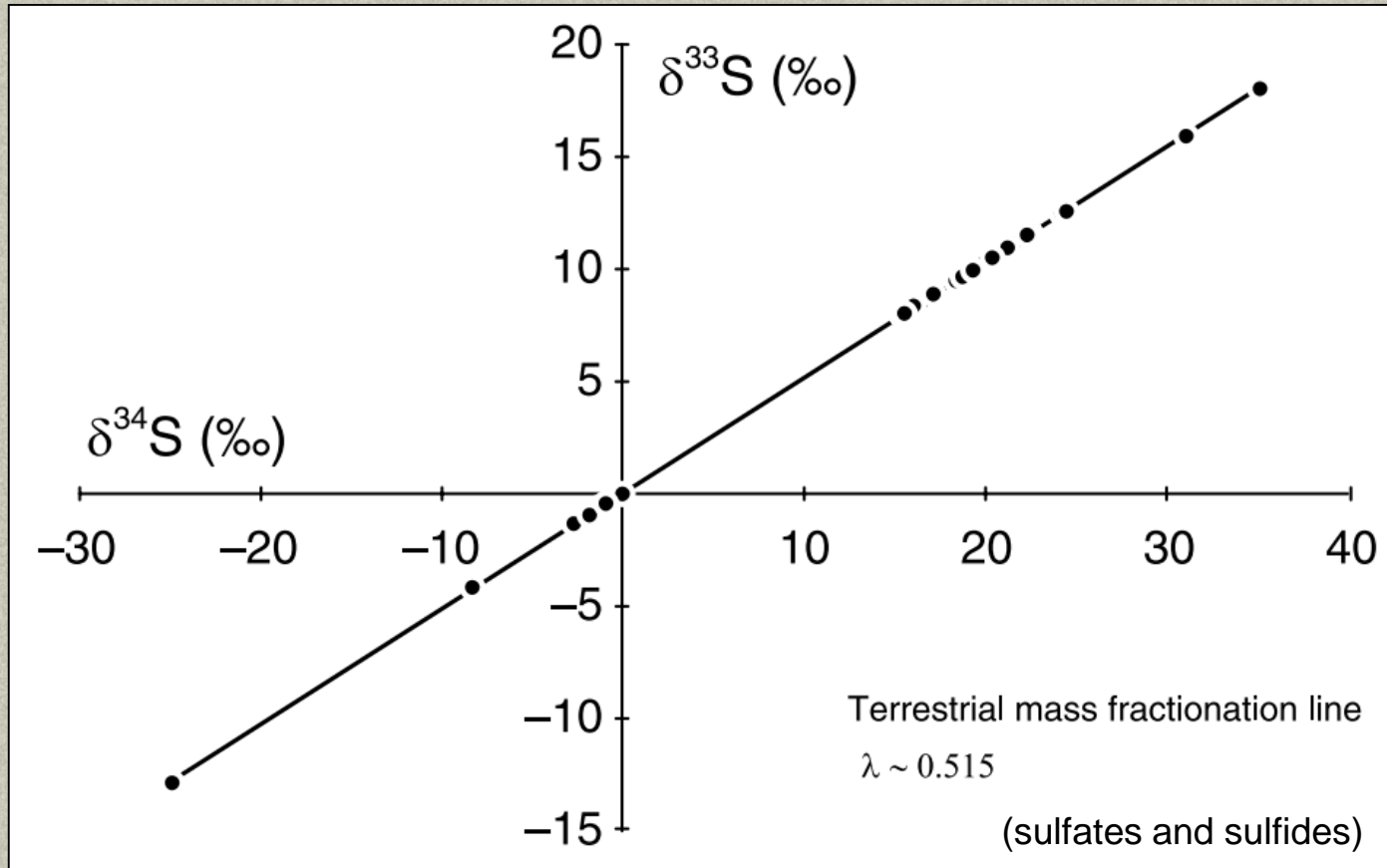
$$\delta^m \text{S} = \left[\frac{\left(\frac{{}^m \text{S}}{{}^{32} \text{S}} \right)_{\text{sample}}}{\left(\frac{{}^m \text{S}}{{}^{32} \text{S}} \right)_{\text{reference}}} - 1 \right] \times 1000$$

$$m = 33, 34, 36$$

WHY SULFUR ISOTOPES ?

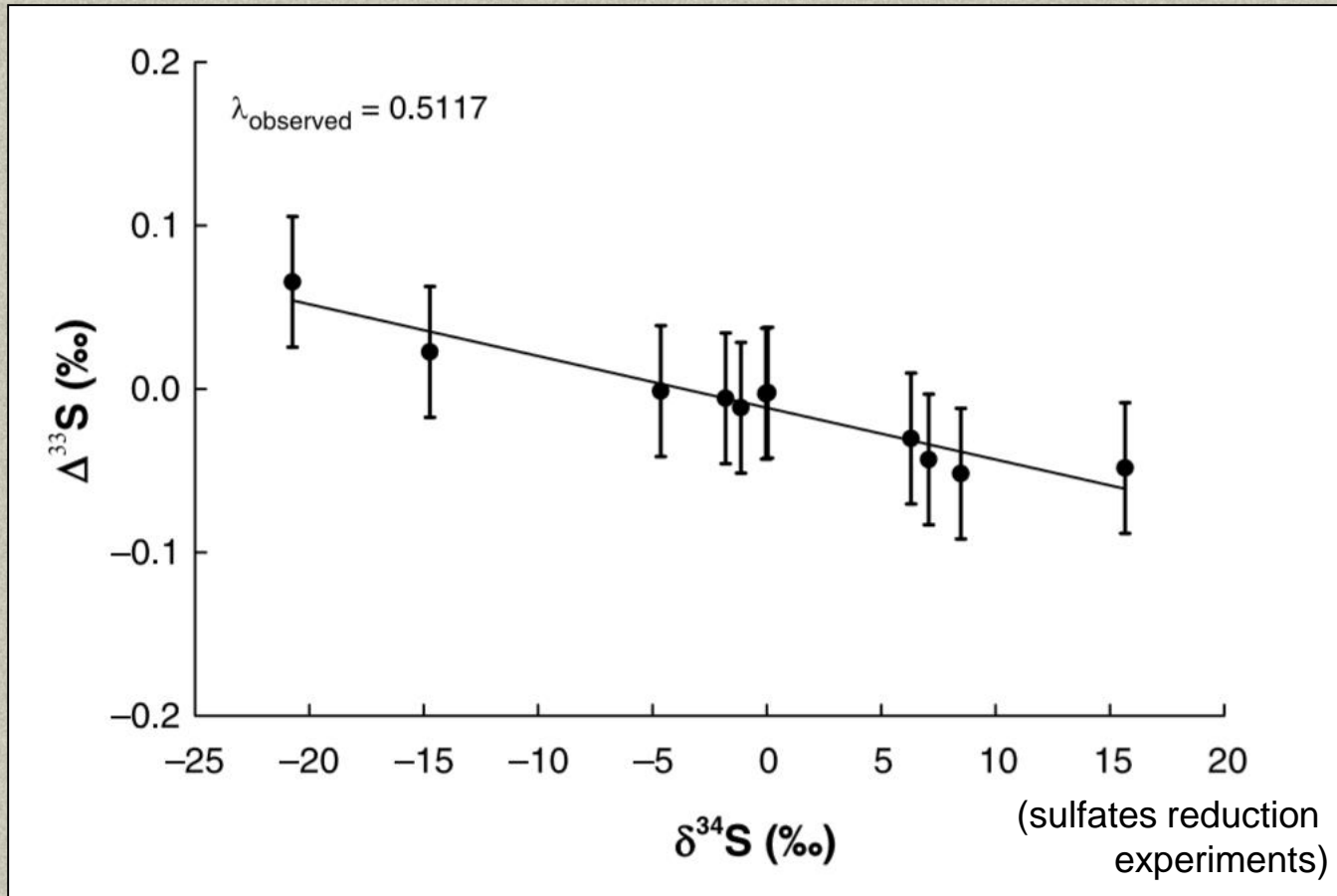


SULFUR MASS-DEPENDENT FRACTIONATION (MDF)



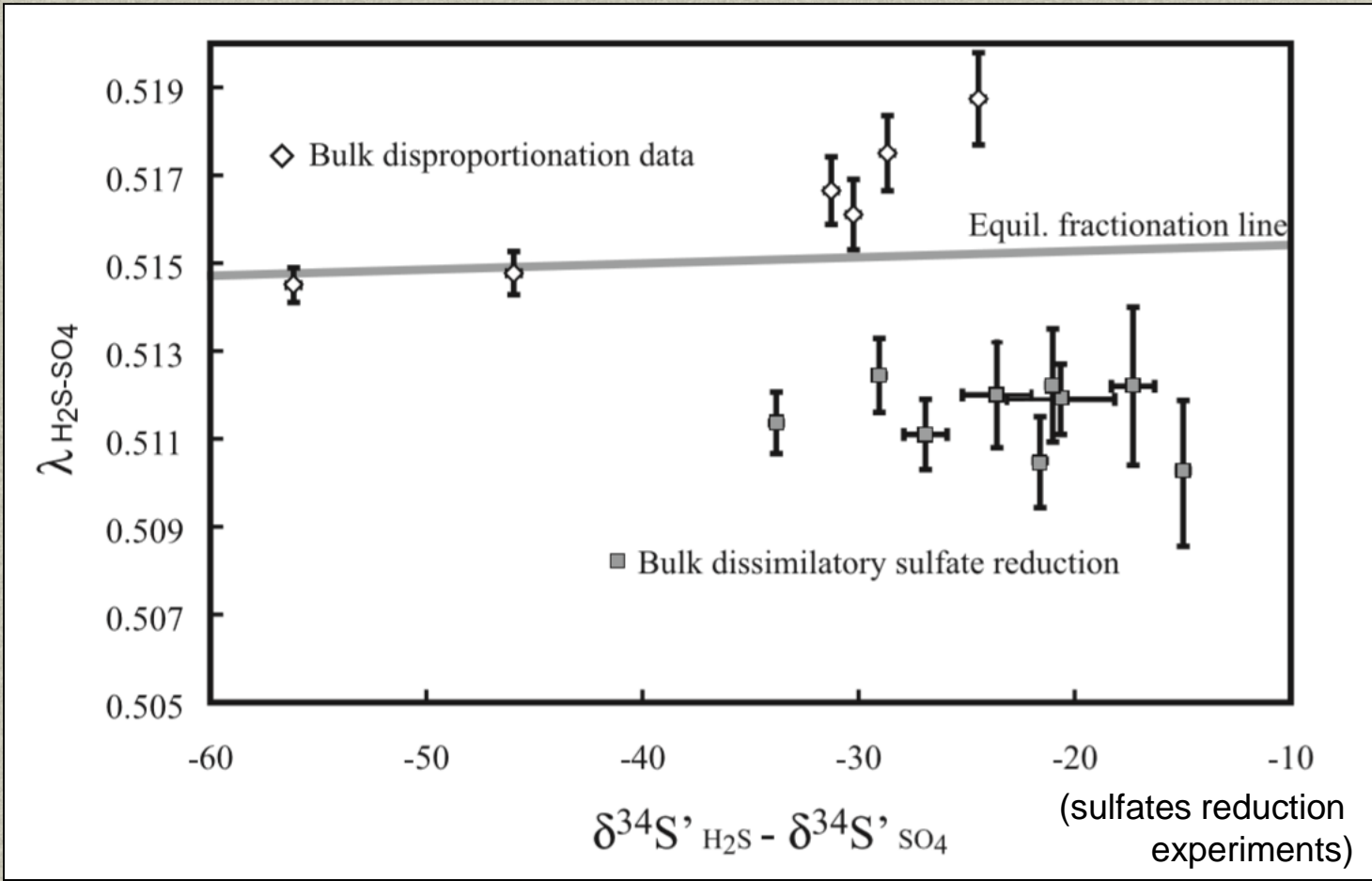
$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times \left[\left(1 + \delta^{34}\text{S} \right)^{0.515} - 1 \right]$$

SULFUR ANOMALOUS MDF



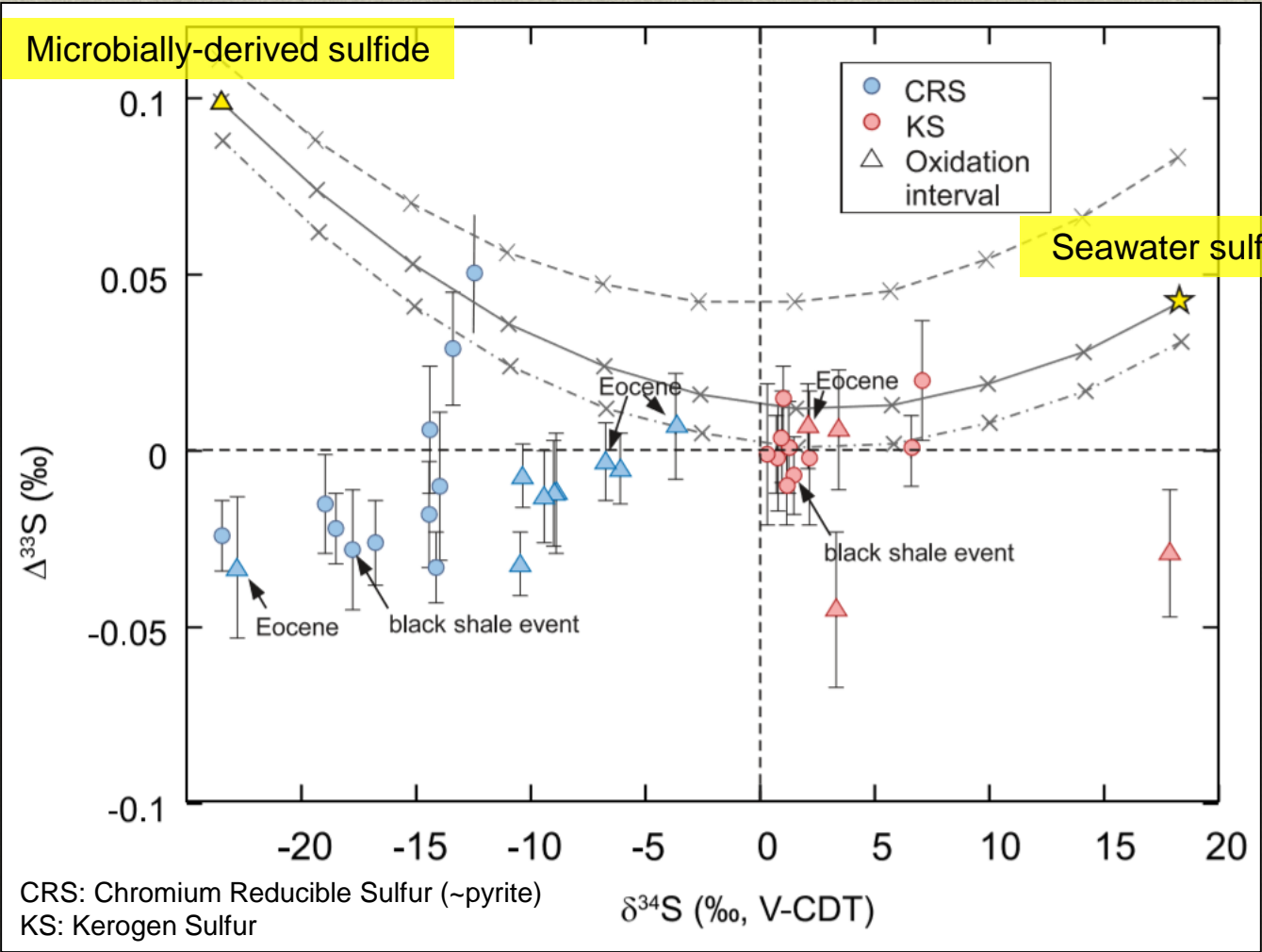
$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times \left[\left(1 + \delta^{34}\text{S} \right)^{0.515} - 1 \right]$$

SULFUR ANOMALOUS MDF

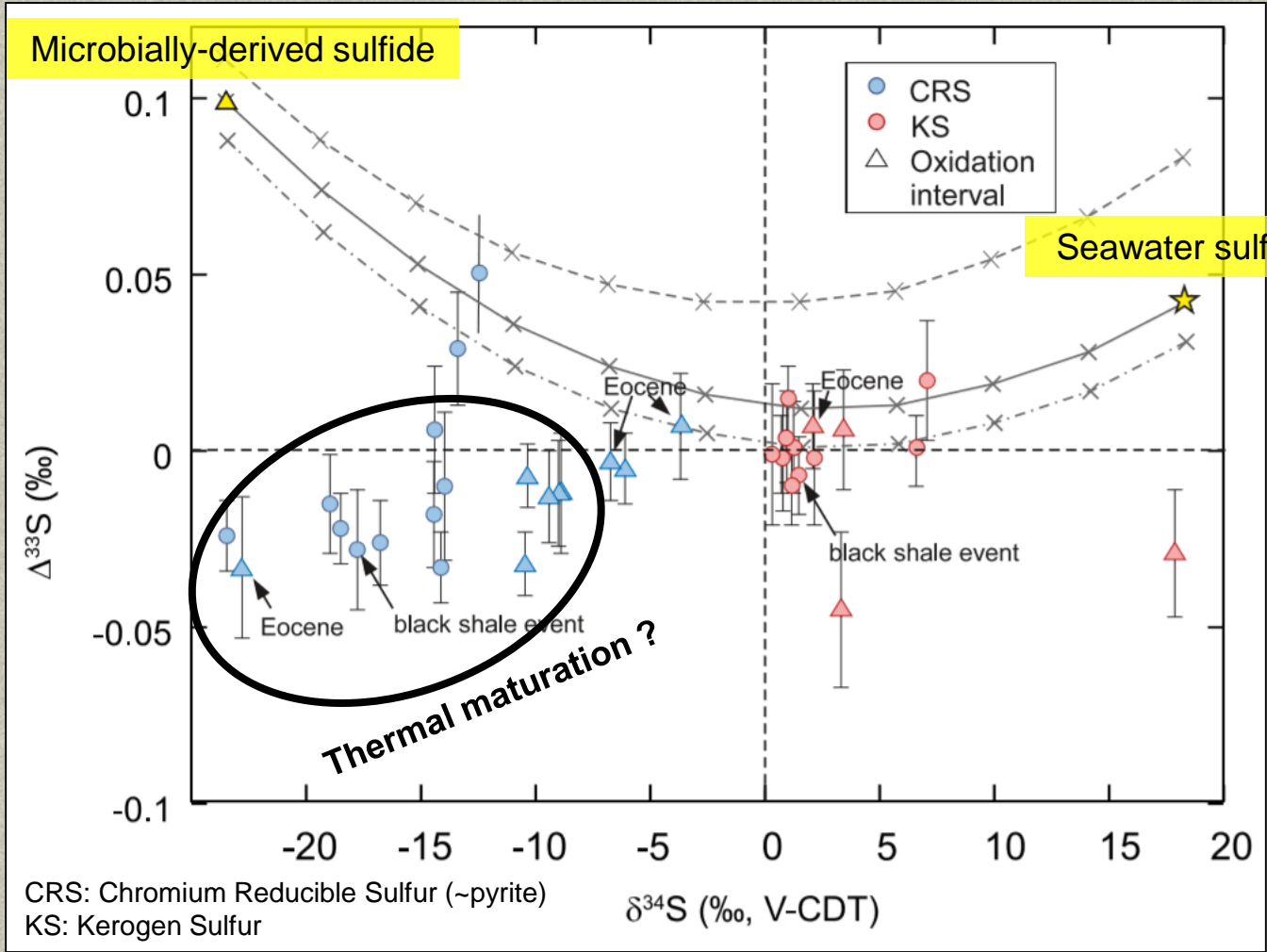


Source: Johnston *et al.* (2005), including Farquhar *et al.* (2003)

SULFUR ANOMALOUS MDF



SULFUR ANOMALOUS MDF



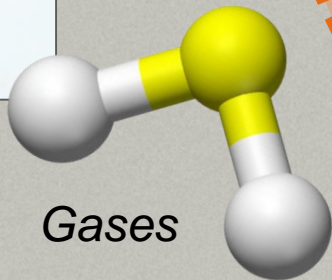
MAIN FORMS OF SULFUR COMPOUNDS



Sulfates



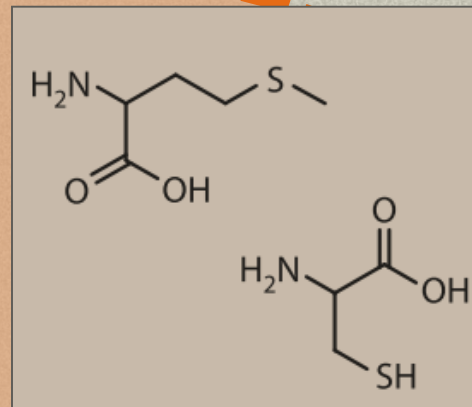
Sulfides



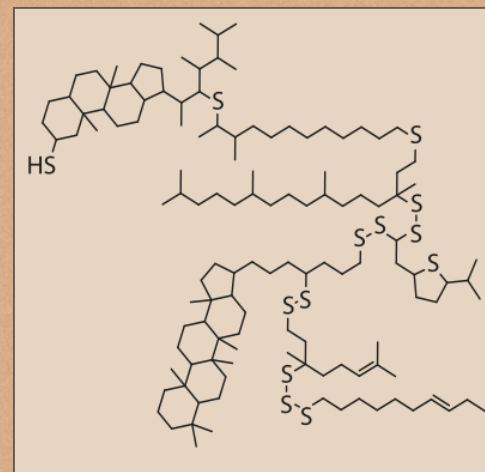
Gases



Elemental sulfur



Biosynthetic S-compounds



Sulfurized compounds

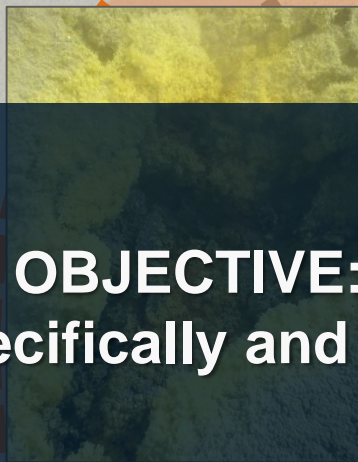
Inorganic

Organic

MAIN FORMS OF SULFUR COMPOUNDS

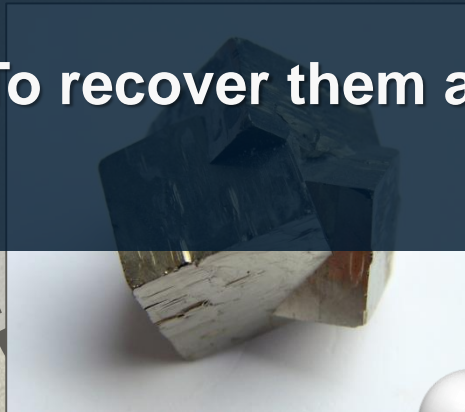


Sulfates

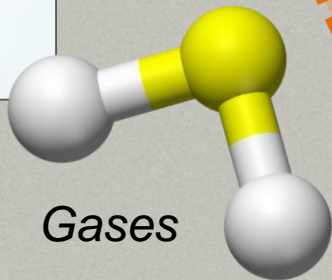


OBJECTIVE:

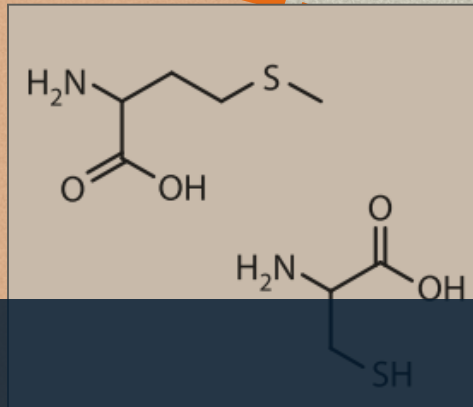
To recover them all as specifically and quantitatively as possible.



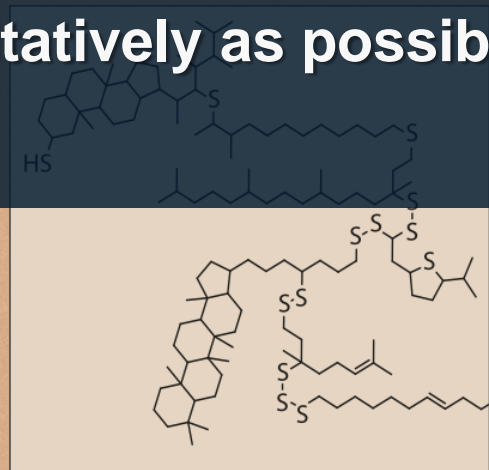
Sulfides



Gases



Biosynthetic S-compounds



Sulfurized compounds

Inorganic

Organic

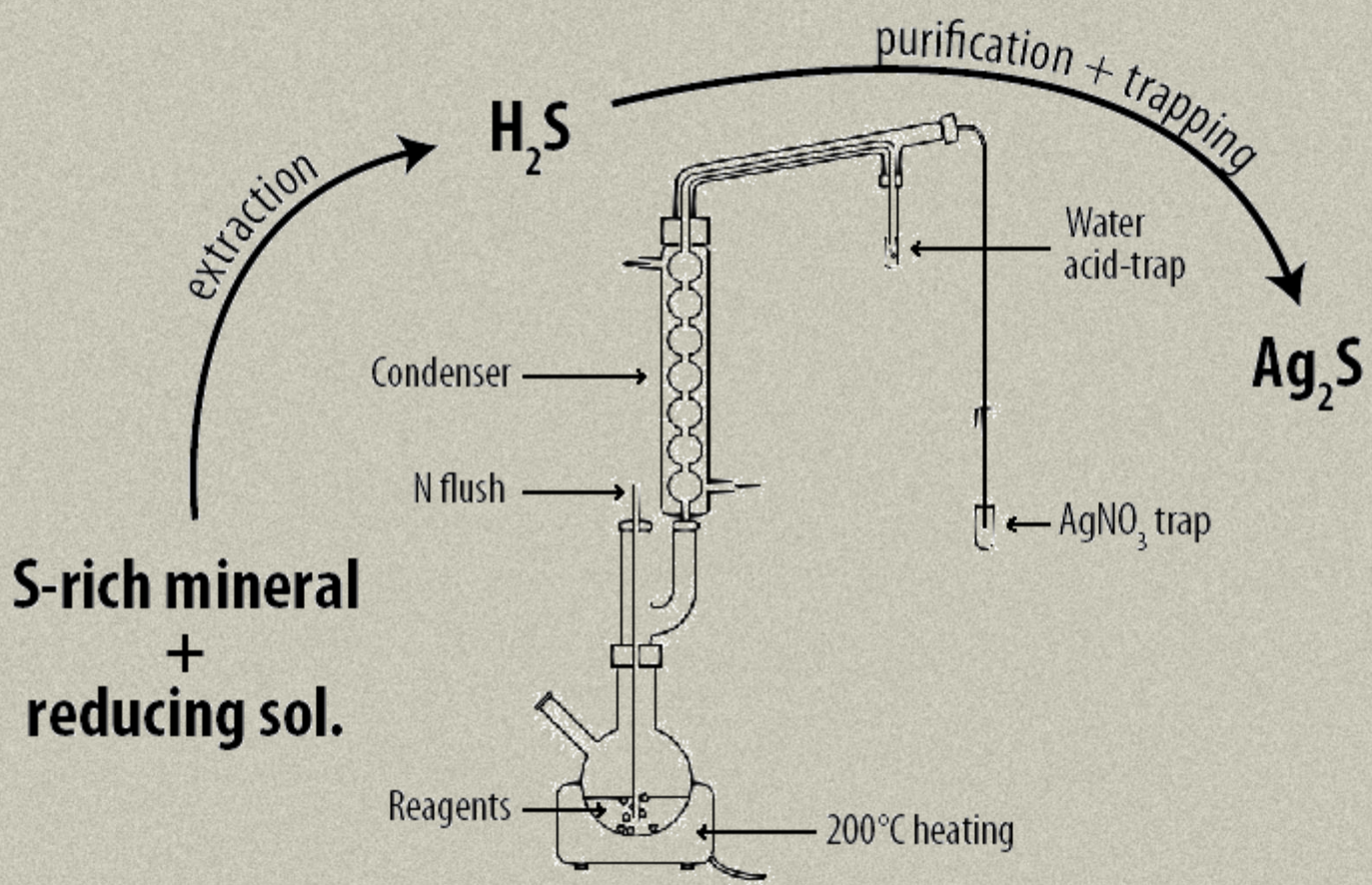
MATERIAL & METHODS

SULFUR COMPOUNDS STUDY: ANALYTICAL APPROACHES



Many techniques have been developed and used. However, none allows to get quantitative and specific multi-isotopic values for all sulfur pools from a single sample.

SULFUR DISTILLATION: PRINCIPLE



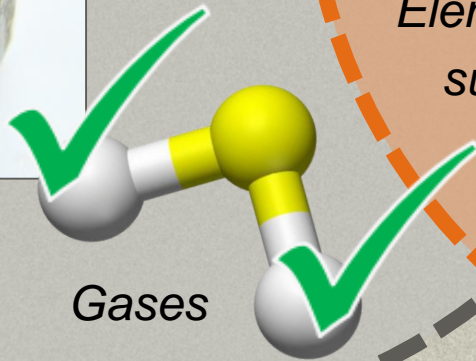
EASILY DISTILLABLE SULFUR COMPOUNDS



Sulfates



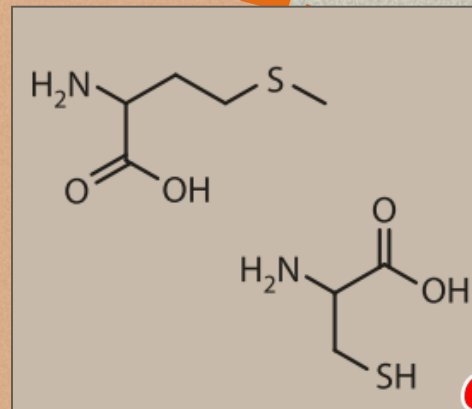
Sulfides



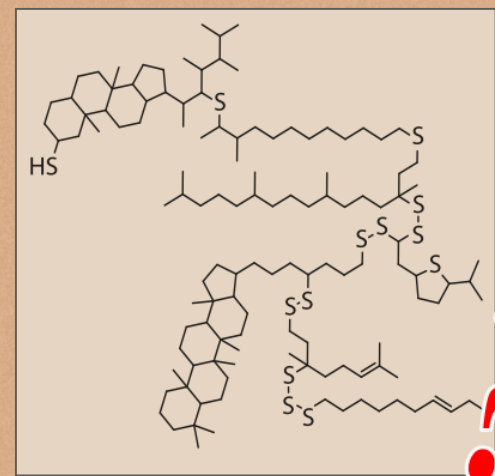
Gases



Elemental sulfur



Biosynthetic S-compounds

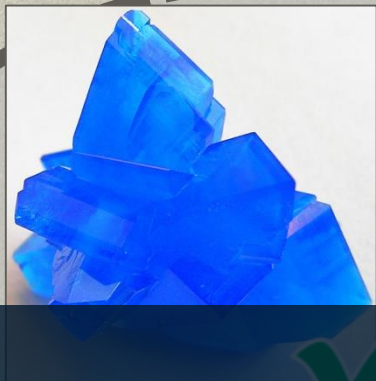


Sulfurized compounds

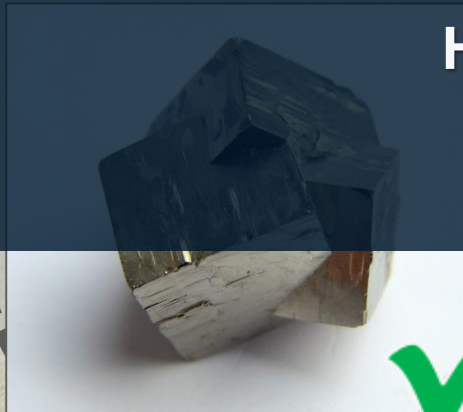
Inorganic

Organic

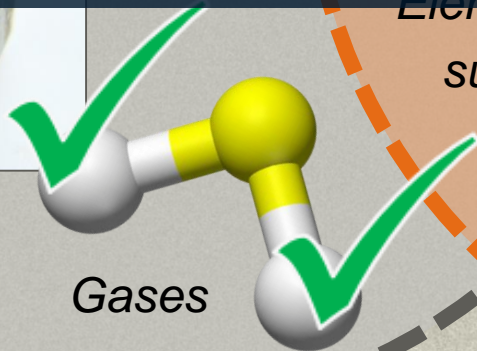
EASILY DISTILLABLE SULFUR COMPOUNDS



Sulfates



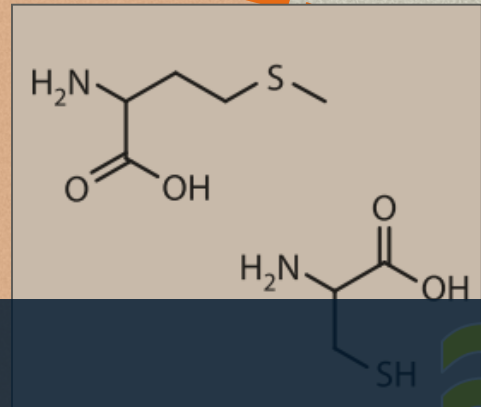
Sulfides



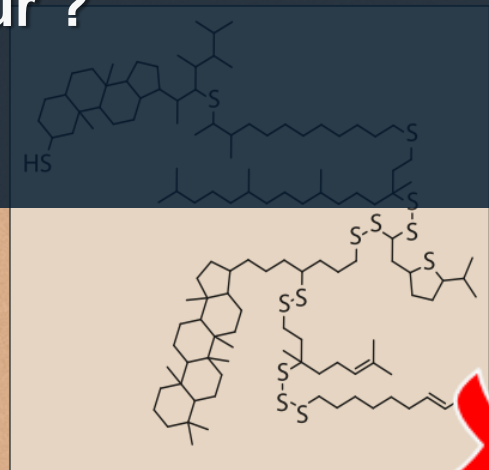
Gases



Elemental sulfur



Biosynthetic S-compounds



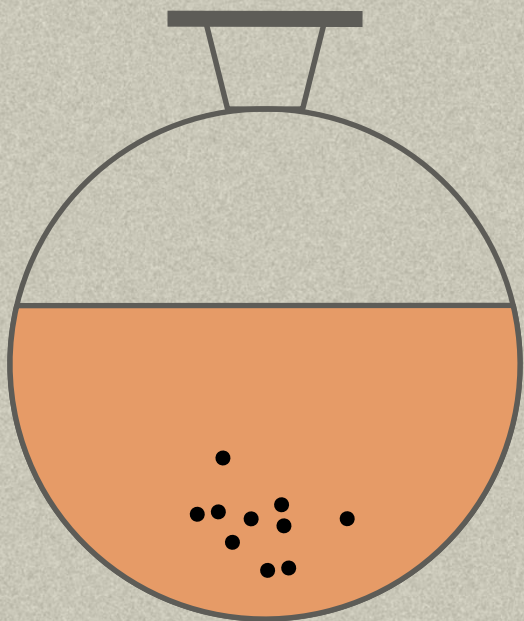
Sulfurized compounds

Inorganic

Organic

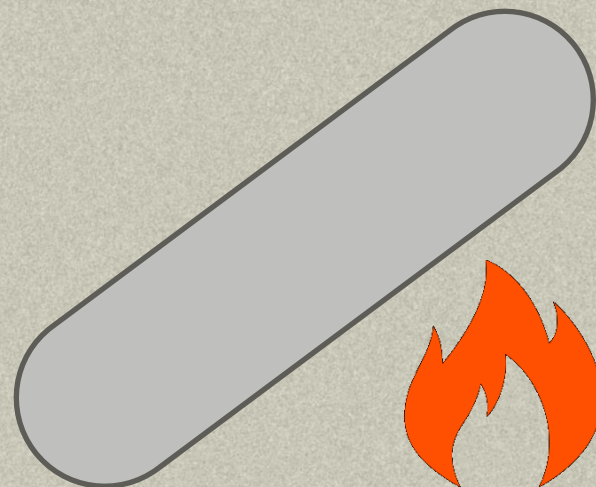
How to recover organic sulfur ?

ORGANIC SULFUR EXTRACTION: EXISTING METHODS



Raney Nickel Desulfurization

Non quantitative



Parr bomb/Eschka powder oxidation

Technically complex

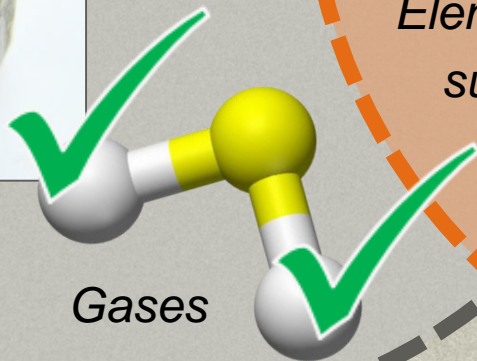
EASILY DISTILLABLE SULFUR COMPOUNDS



Sulfates



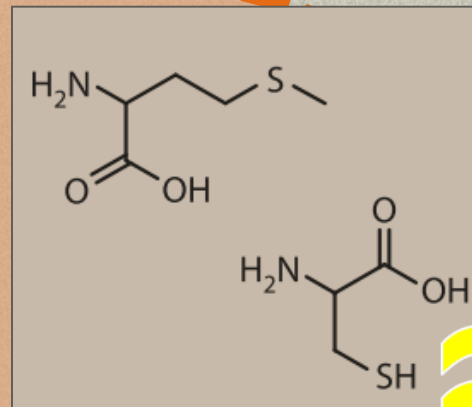
Sulfides



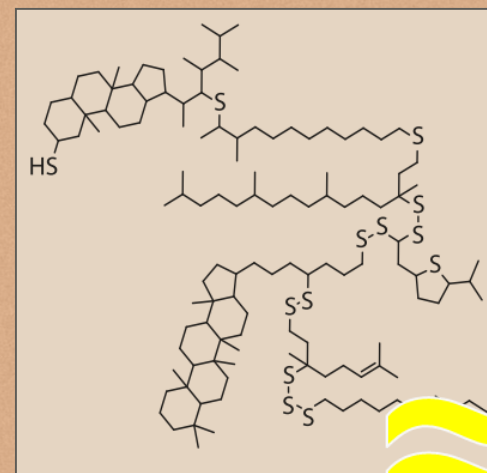
Gases



Elemental sulfur



Biosynthetic S-compounds



Sulfurized compounds

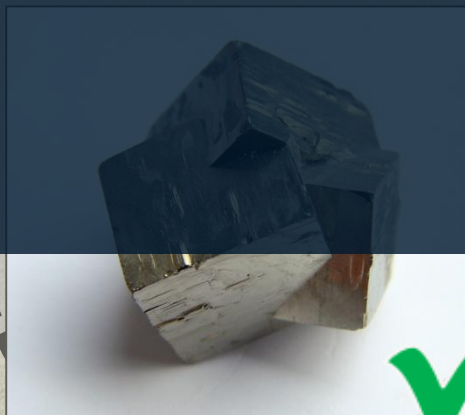
Inorganic

Organic

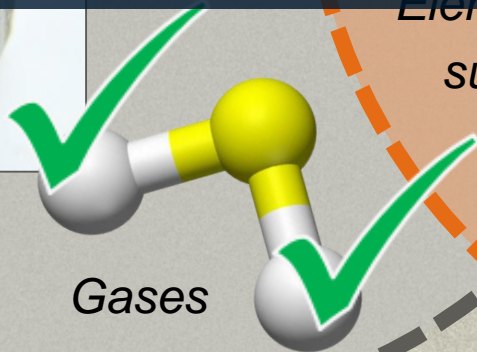
EASILY DISTILLABLE SULFUR COMPOUNDS



Sulfates



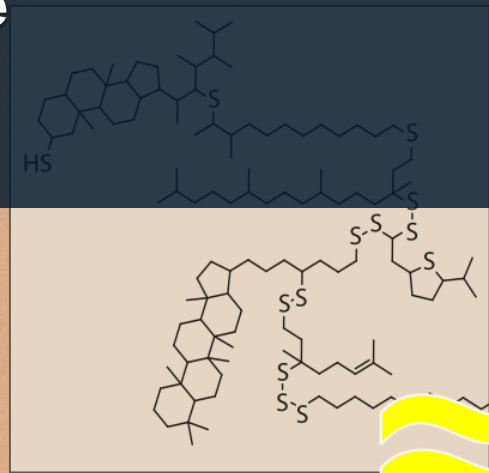
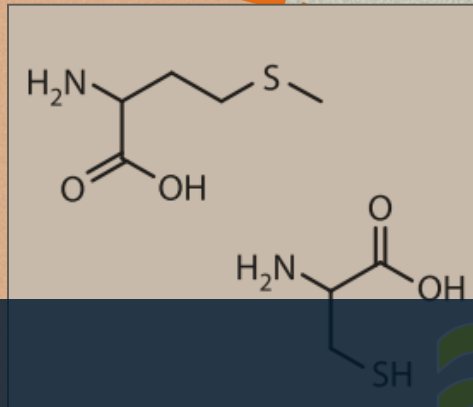
Sulfides



Need for a new procedure



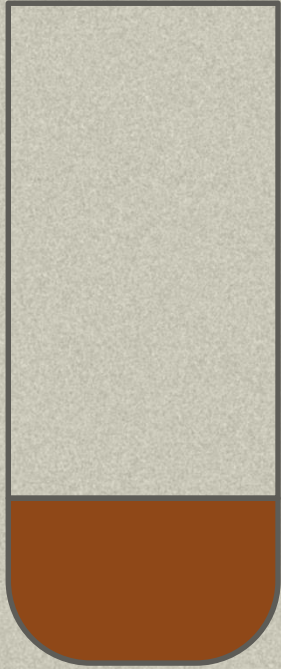
Elemental sulfur



Inorganic

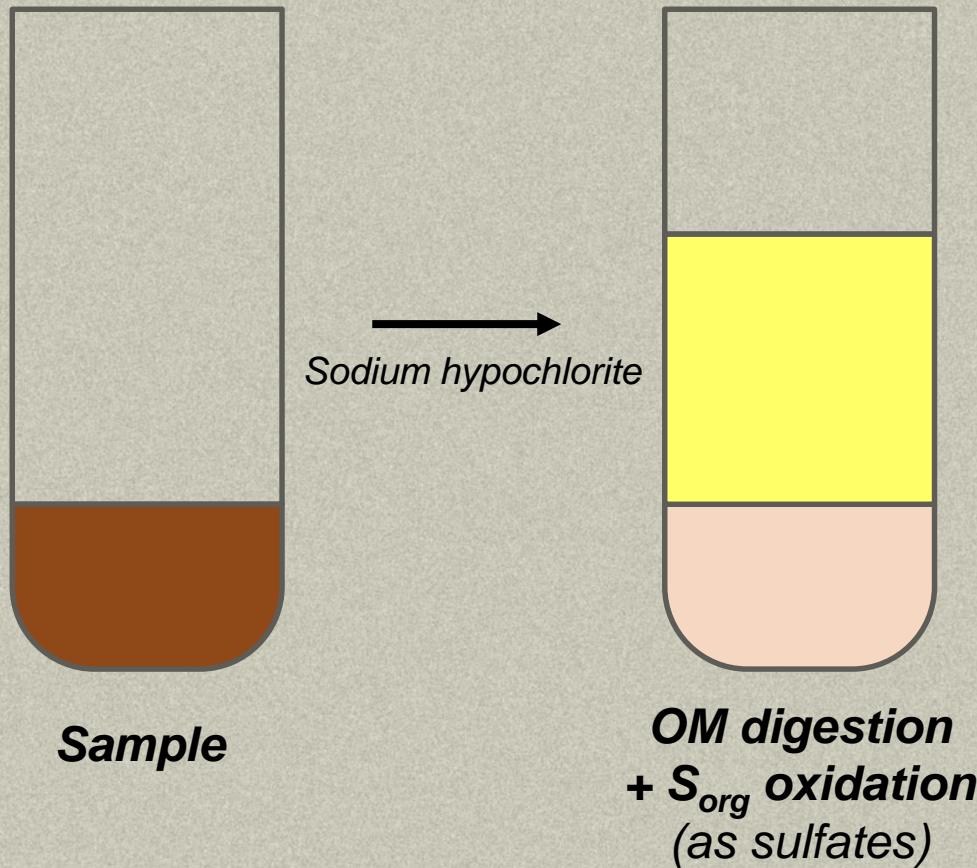
Organic

ORGANIC SULFUR EXTRACTION: NEW METHOD

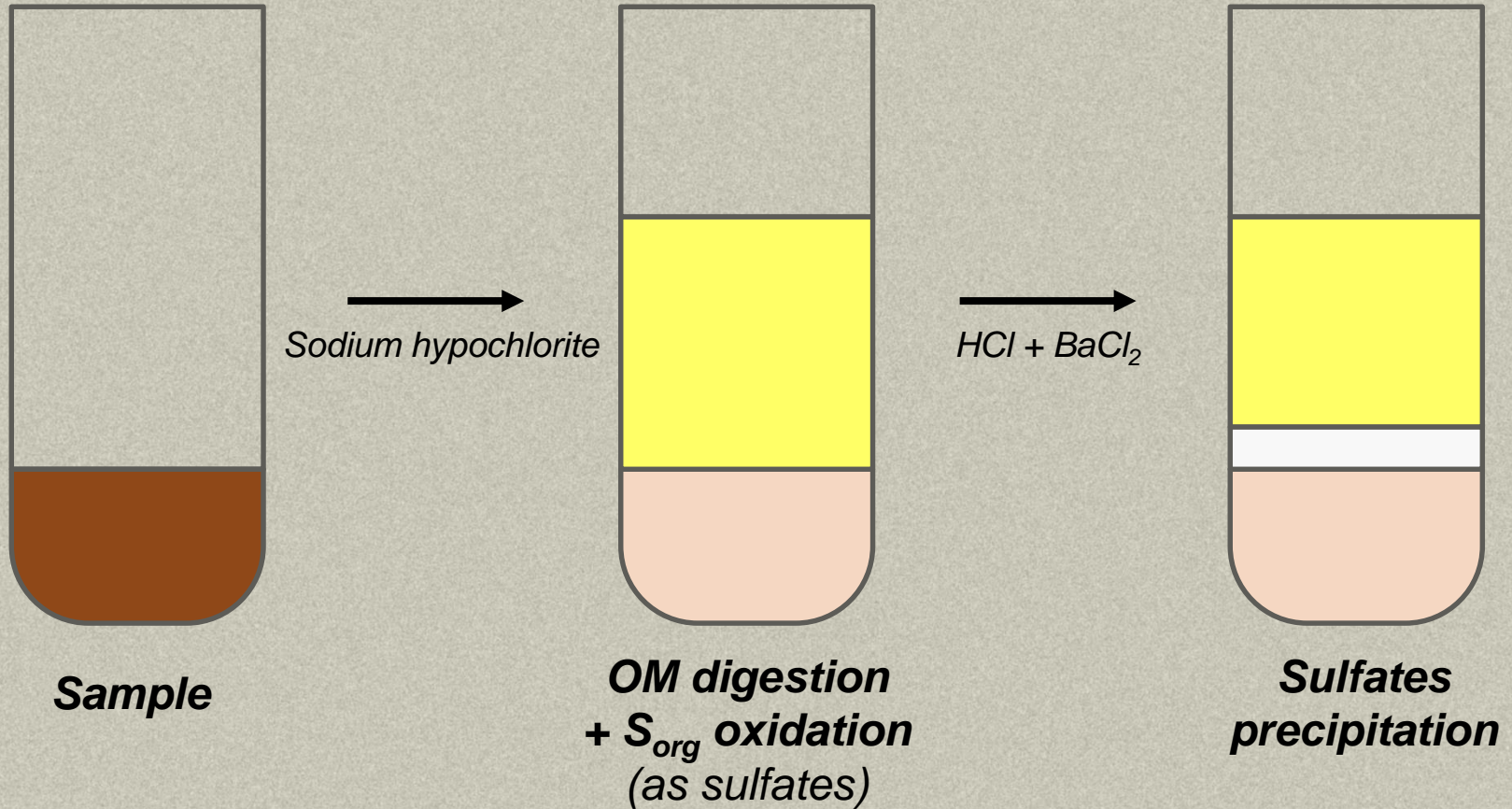


Sample

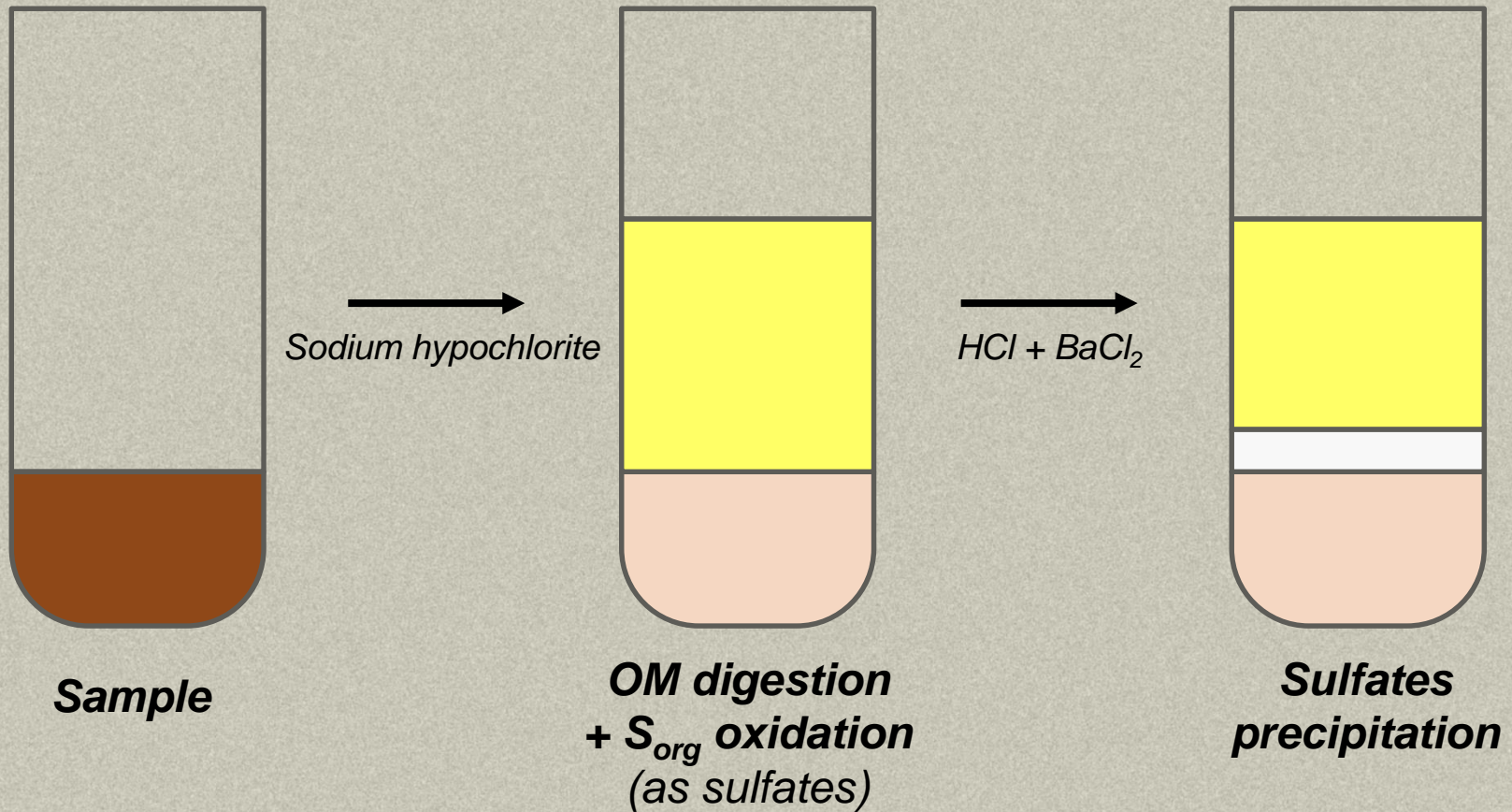
ORGANIC SULFUR EXTRACTION: NEW METHOD



ORGANIC SULFUR EXTRACTION: NEW METHOD

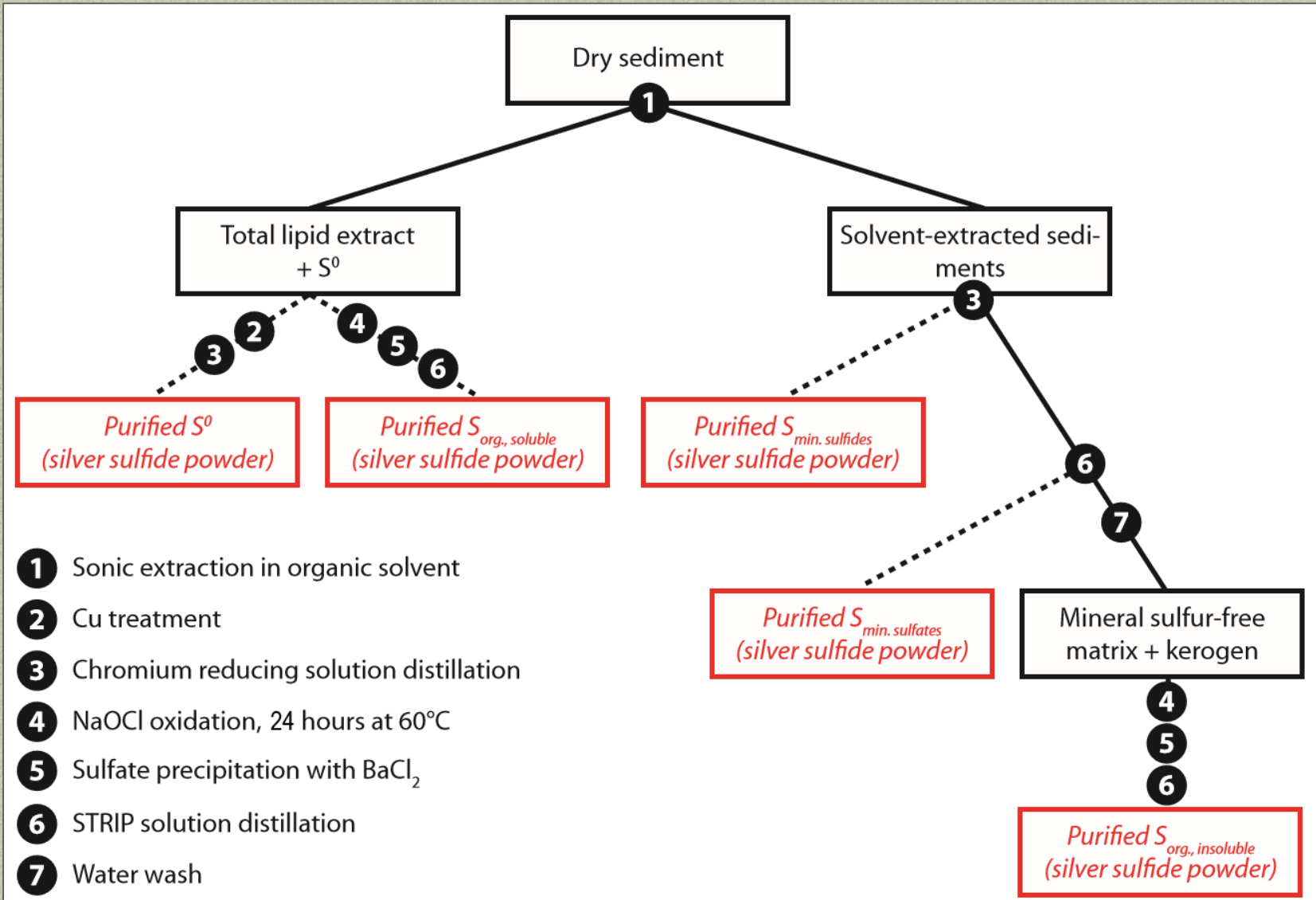


ORGANIC SULFUR EXTRACTION: NEW METHOD



Precipitated sulfates can easily be extracted with STRIP solution distillation.

INTEGRATED WORKFLOW



SAMPLES



Lake Dziani Dzaha (Mayotte); TOC~10%



Rozel Point Oil (USA); TOC~50%



Green River Fm (USA); TOC~28%

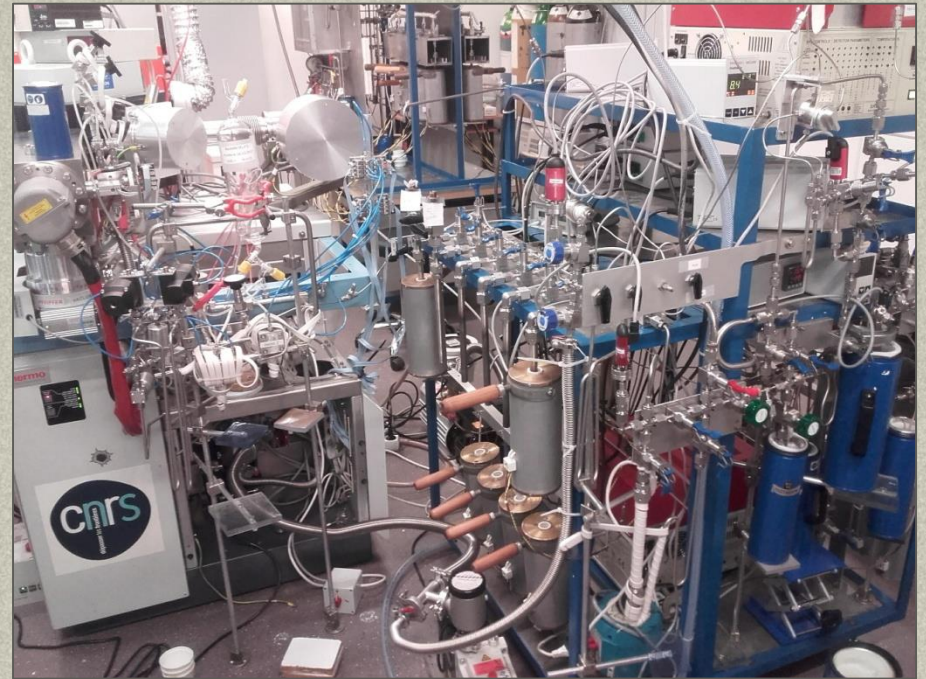


Limagne (Auvergne); TOC~13%

ANALYTICAL EQUIPMENT



Elementar Cube CS (ISA Lyon)



F₂-IRMS (Thermo MAT253, IPG Paris)

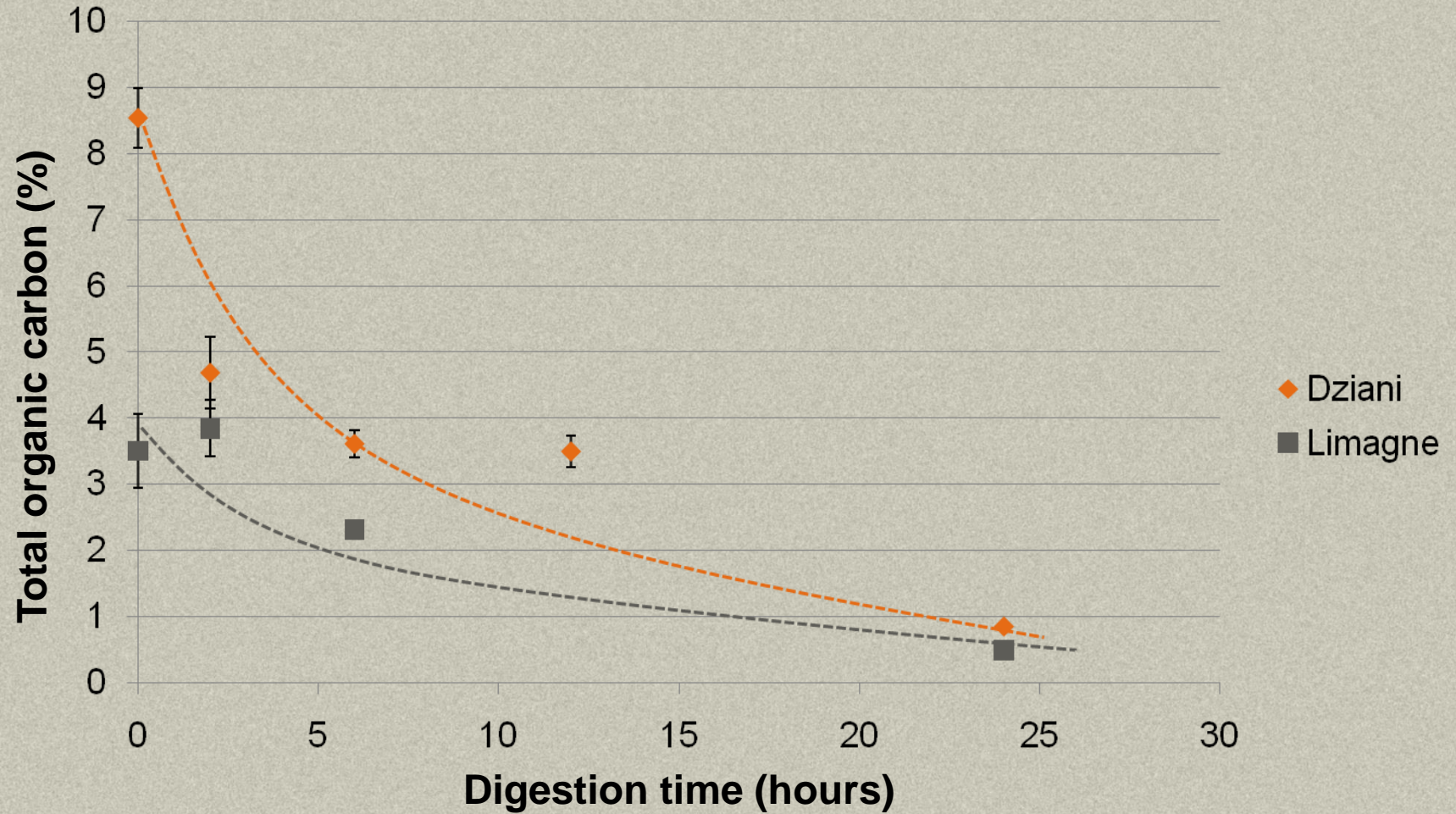


Elementar Vario Isotope Cube (LGL)

RESULTS & DISCUSSION

OM DIGESTION KINETICS

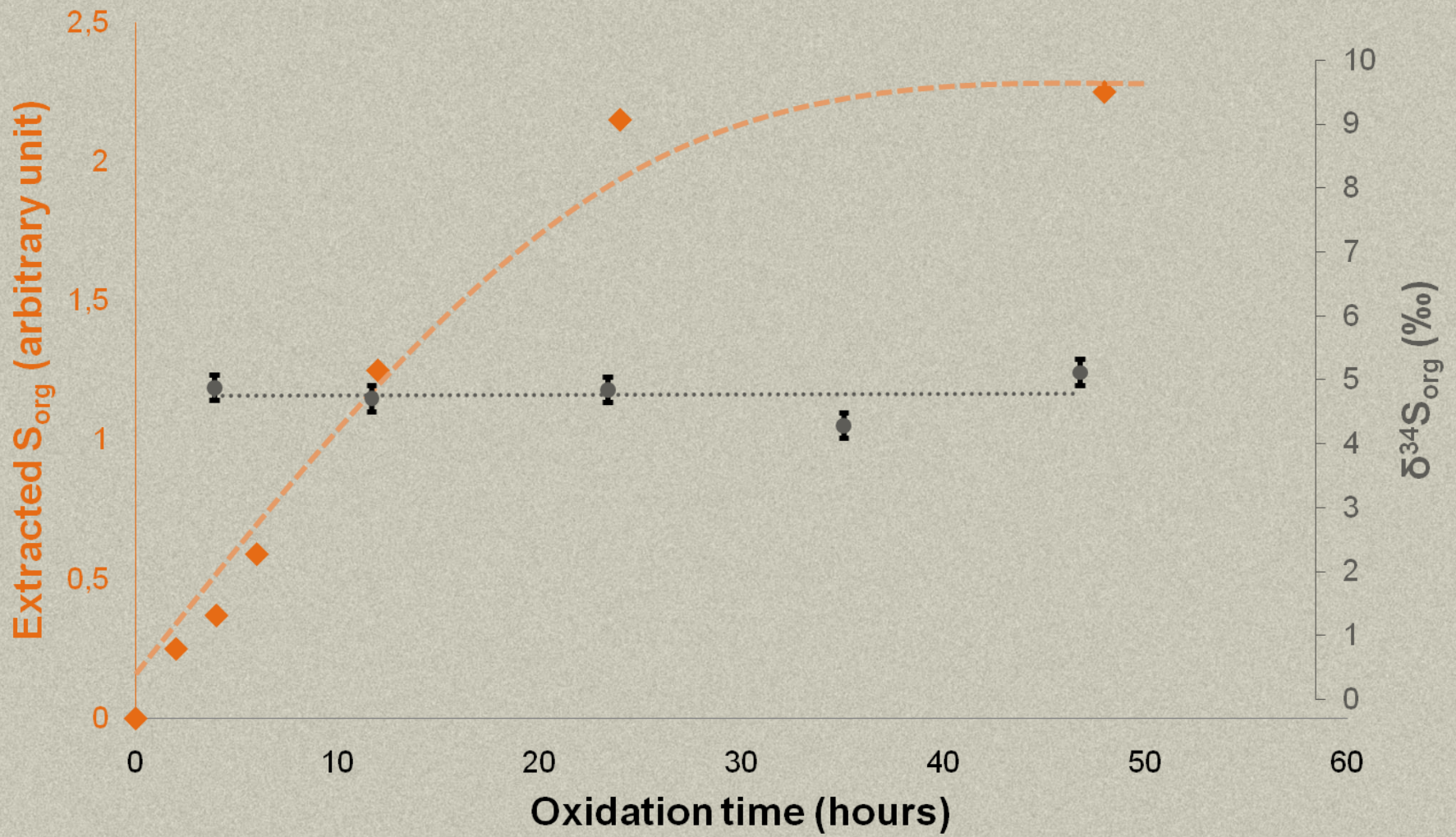
OM DIGESTION KINETICS



OM DIGESTION KINETICS



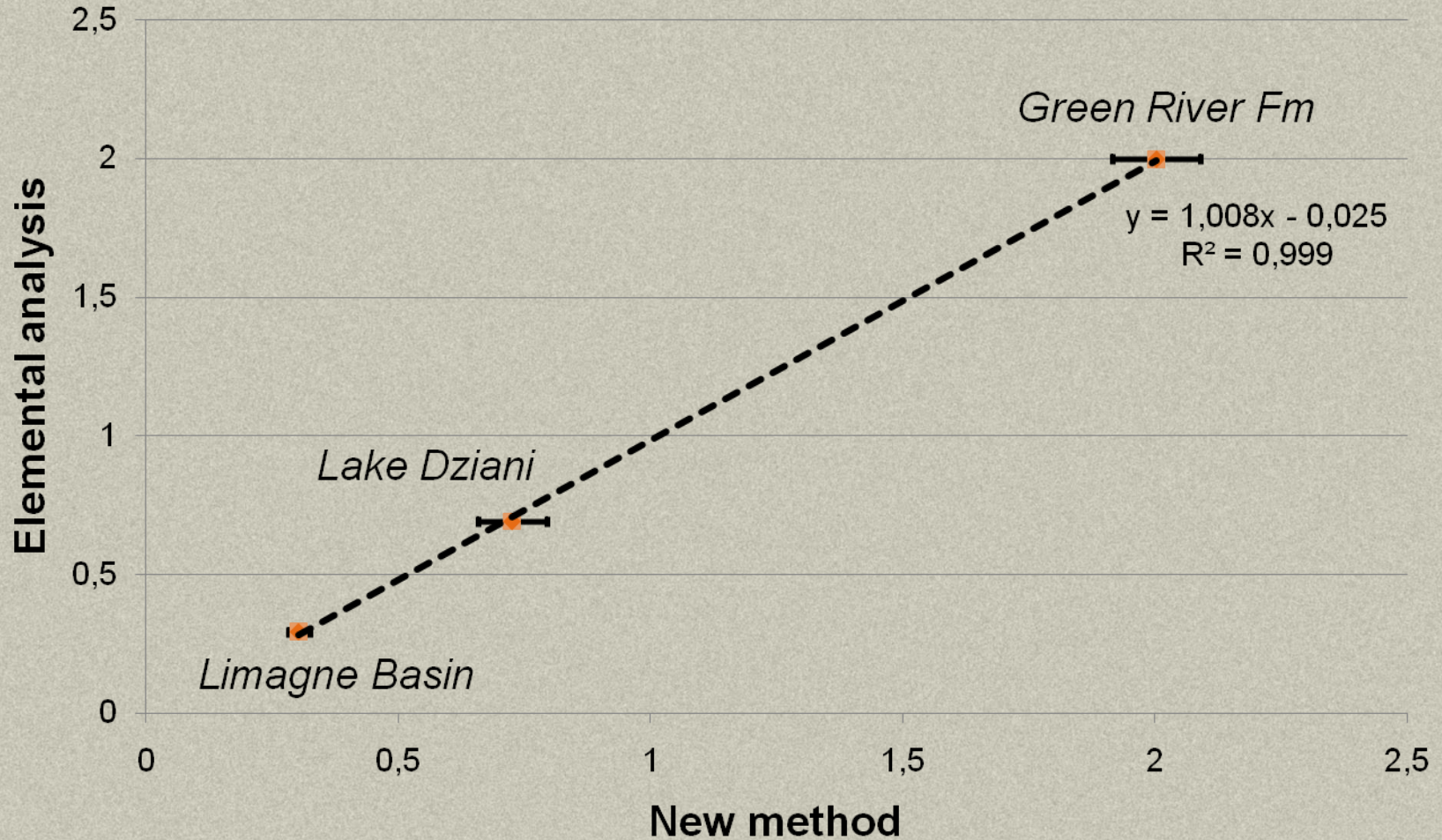
OM DIGESTION KINETICS



SULFUR RECOVERY EVALUATION

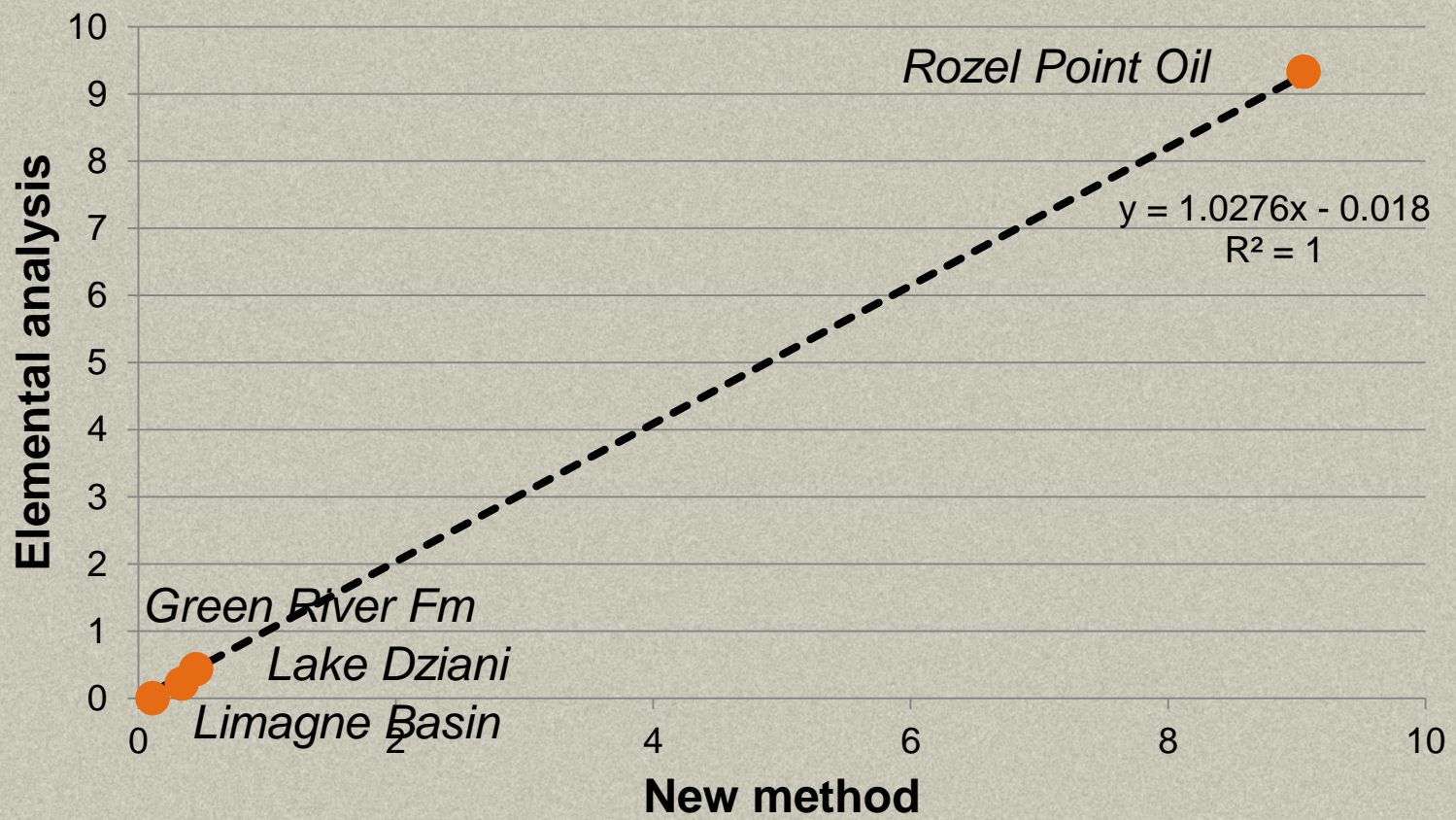
SULFUR RECOVERY EVALUATION

Bulk sulfur content evaluation (wt%S)

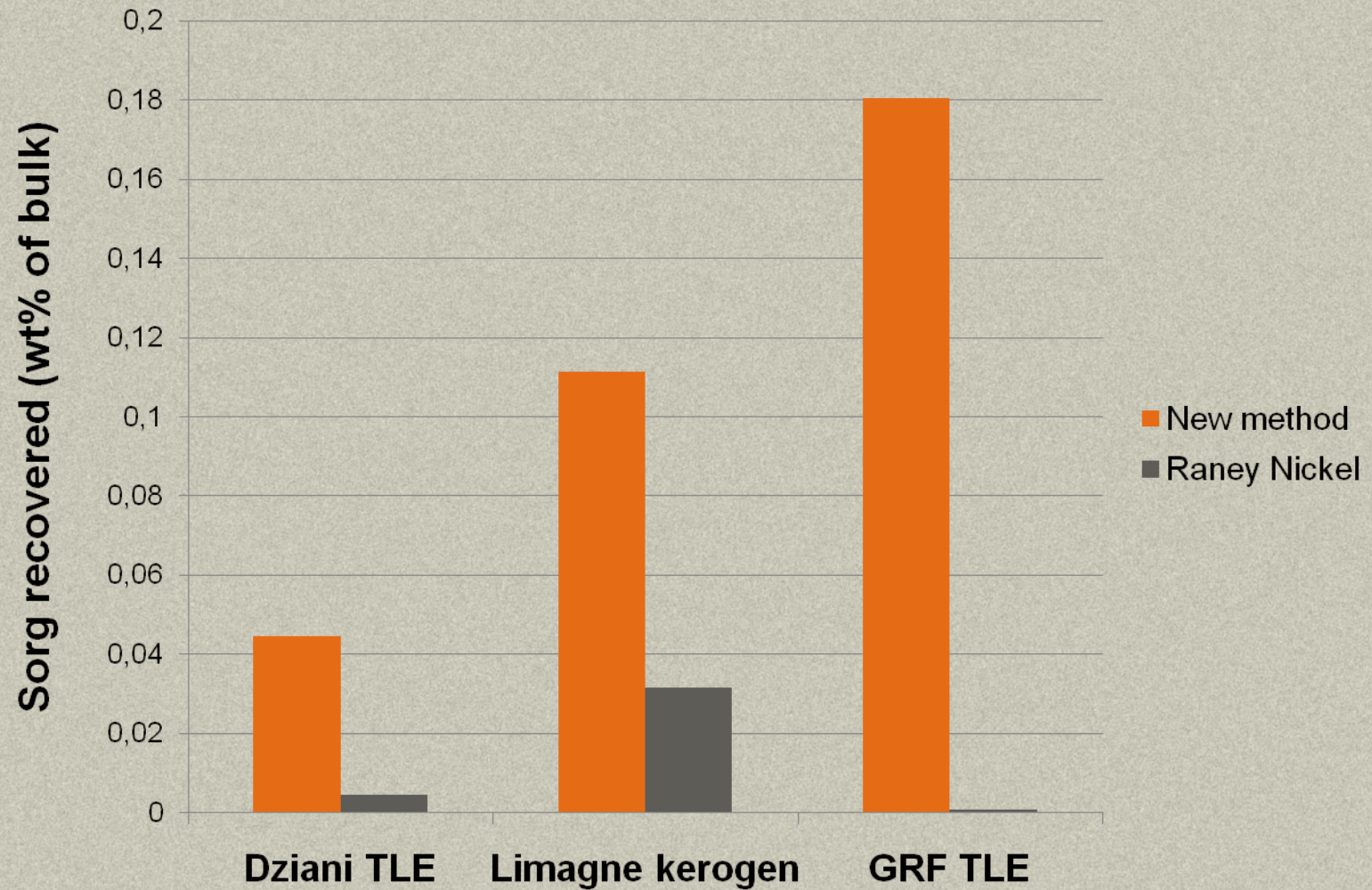


SULFUR RECOVERY EVALUATION

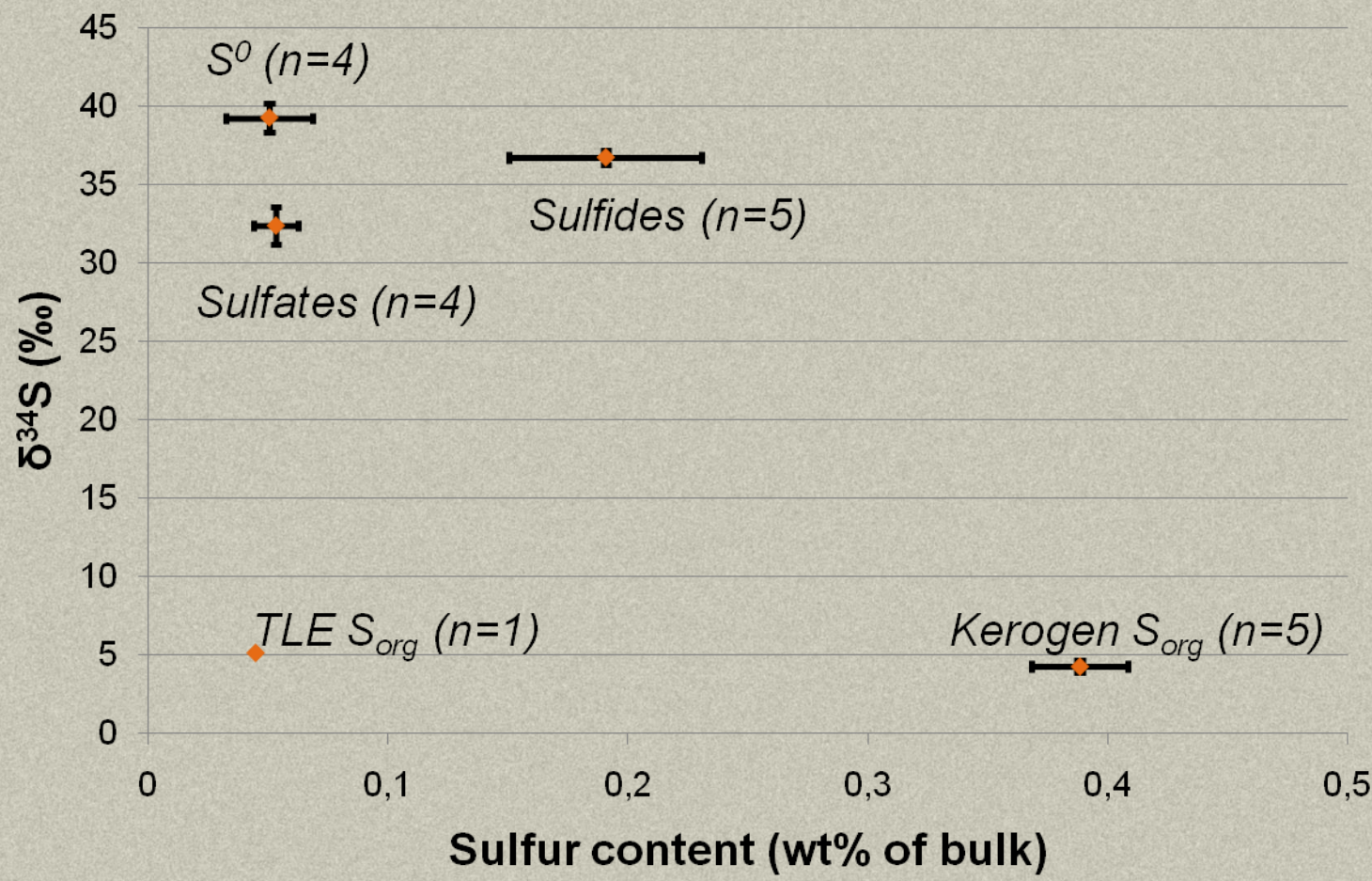
Organic matter sulfur content evaluation (wt%S)



SULFUR RECOVERY: RANEY NICKEL



METHOD REPLICABILITY (LAKE DZIANI)

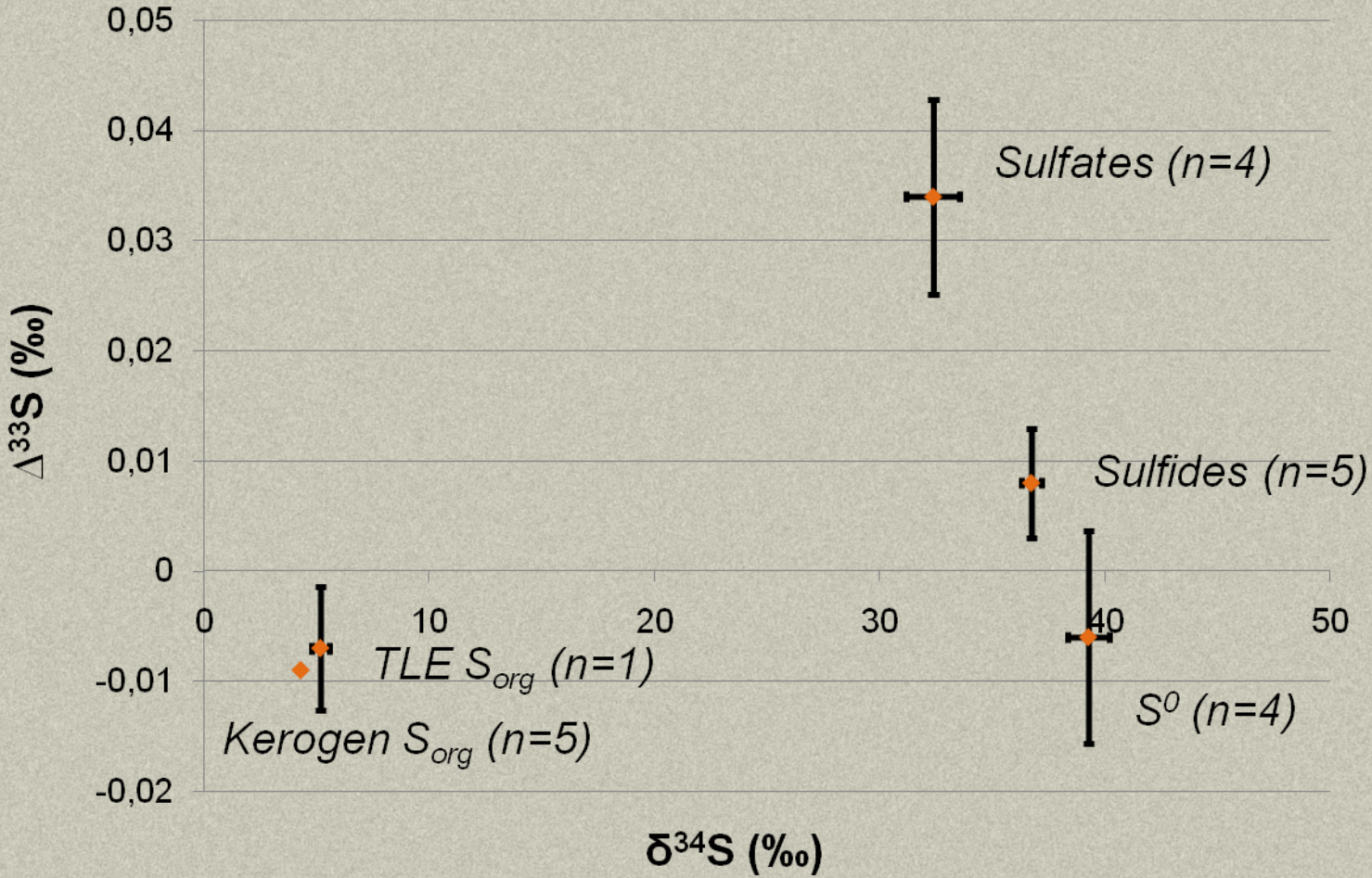


Total sulfur content: 0.73%

Org. sulfur content: 0.43%

$S_{org}/S_{total}=0.59$

SULFUR MULTI-ISOTOPY (LAKE DZIANI)



PERSPECTIVES: A SHORT PREVIEW

THE CASE OF THE GREEN RIVER FM

Tuttle & Goldhaber (1991)*

- $S_{\text{total}} = 1.5 \pm 0.5\%$

This study

- $S_{\text{total}} = 2.0 \pm 0.09\%$

THE CASE OF THE GREEN RIVER FM

Tuttle & Goldhaber (1991)*

- $S_{\text{total}} = 1.5 \pm 0.5\%$
- $S_{\text{org}} = 0.3 \pm 0.5\%$

This study

- $S_{\text{total}} = 2.0 \pm 0.09\%$
- $S_{\text{org}} = 0.59 \pm 0.06\%$

THE CASE OF THE GREEN RIVER FM

Tuttle & Goldhaber (1991)*

- $S_{\text{total}} = 1.5 \pm 0.5\%$

- $S_{\text{org}} = 0.3 \pm 0.5\%$

- $S_{\text{org}}/S_{\text{total}} = 0.19 \pm 0.08$

This study

- $S_{\text{total}} = 2.0 \pm 0.09\%$

- $S_{\text{org}} = 0.59 \pm 0.06\%$

- $S_{\text{org}}/S_{\text{total}} = 0.29 \pm 0.03$

THE CASE OF THE GREEN RIVER FM

Tuttle & Goldhaber (1991)*

- $S_{\text{total}} = 1.5 \pm 0.5\%$
- $S_{\text{org}} = 0.3 \pm 0.5\%$
- $S_{\text{org}}/S_{\text{total}} = 0.19 \pm 0.08$
- $\delta^{34}\text{S}_{\text{sulfides}} = 31.6 \pm 4.4\text{‰}$

This study

- $S_{\text{total}} = 2.0 \pm 0.09\%$
- $S_{\text{org}} = 0.59 \pm 0.06\%$
- $S_{\text{org}}/S_{\text{total}} = 0.29 \pm 0.03$
- $\delta^{34}\text{S}_{\text{sulfides}} = 29.71 \pm 0.09\text{‰}$

THE CASE OF THE GREEN RIVER FM

Tuttle & Goldhaber (1991)*

- $S_{\text{total}} = 1.5 \pm 0.5\%$
- $S_{\text{org}} = 0.3 \pm 0.5\%$
- $S_{\text{org}}/S_{\text{total}} = 0.19 \pm 0.08$
- $\delta^{34}\text{S}_{\text{sulfides}} = 31.6 \pm 4.4\text{‰}$
- $\delta^{34}\text{S}_{\text{org}} = 28.7 \pm 1.1\text{‰}$

This study

- $S_{\text{total}} = 2.0 \pm 0.09\%$
- $S_{\text{org}} = 0.59 \pm 0.06\%$
- $S_{\text{org}}/S_{\text{total}} = 0.29 \pm 0.03$
- $\delta^{34}\text{S}_{\text{sulfides}} = 29.71 \pm 0.09\text{‰}$
- $\delta^{34}\text{S}_{\text{org}} = 4.85 \pm 0.05\text{‰}$

TAKE HOME MESSAGES

- Sulfur isotopes can unveil biogeochemical cycles processes;
- This new method allows a multi-pool, multi-isotope approach;
- It is complementary to bulk and compound-specific methods;
- Multi-pool, multi-isotope approaches might bring new keys of interpretation to old case studies.

Acknowledgements: B. Killingsworth and A. Bouyon, for their precious suggestions and assistance in this work. Thank you !

