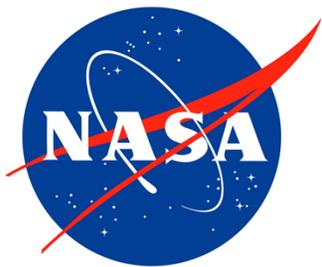


1

Triple oxygen isotope data characterize oxidation processes that produce sulfate on Earth (and Mars?)

Justin Christensen, Issaku Kohl, Max Coleman



Jet Propulsion Laboratory
California Institute of Technology



Slide 1

1

Put names in the same order as on the Abstract

Logos added but not sure if Doc Review will allow them as they are

Also turned Mars from an ellipse to a circle

Max Coleman, 11/16/2011



Mars

- Past life?
- Iron and Sulfate Present



Sulfate at Meridiani Planum



Río Tinto

“Red River”

- Active oxidation of pyrite sulfur to sulfate
- Extremophile microbiology- *Acidithiobacillus ferrooxidans* (Af) & *Leptospirillum ferrooxidans* (Lf)
- Acidic waters



Slide 3

2

Added Lf

Max Coleman, 11/16/2011

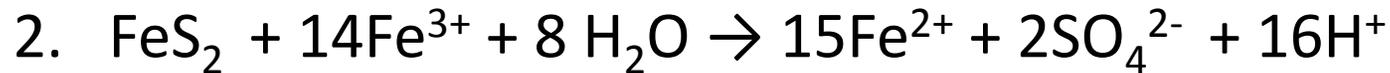


Project Goals

- Identify biomarkers in sulfates
- Determine oxidation pathway of pyrite sulfur to sulfate
- Use triple oxygen isotopes as a tracer for source oxygen



Oxidation Pathways



Microbes Oxidize Sulfur

- High $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios
- Equation 1 more active in pyrite oxidation
- More atmospheric oxygen incorporated into sulfate

Microbes Oxidize Fe^{2+}

- Low $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios
- Equation 2 dominates oxidation pathway
- Quantitative incorporation of water oxygen into sulfate

Slide 5

3

Did you intend to have a shadow on the title?

Max Coleman, 11/16/2011



Definitions

- Isotopes are measured as ratios, least abundant divided by most abundant (i.e. $^{18}\text{O}/^{16}\text{O}$)
- Ratio measured relative to internationally accepted standard
- Reported per mil with delta notation δ , Δ
- $\delta^{18}\text{O} = (R_{\text{Sample}}/R_{\text{Standard}} - 1)1000$
- Allows for both positive (heavier) and negative (lighter) values



Stable Isotope Fractionation

- Stable isotope fractionation is a change in the ratio of the measured isotope
- Occurs during equilibrium and kinetic processes

Mass Dependent

The change in the ratio of one isotope is proportional to the change in the ratio of another by the difference of their masses.

Mass Independent

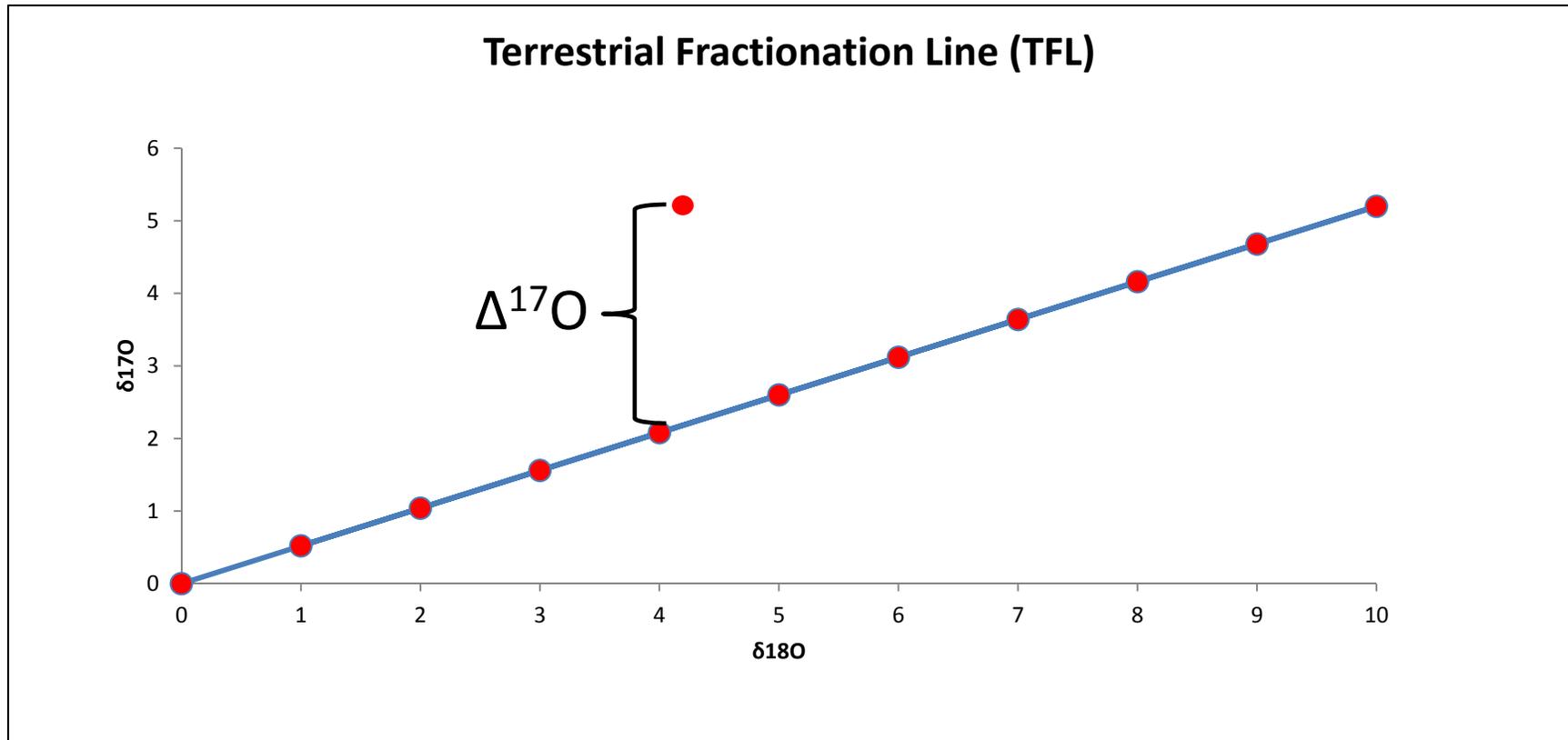
The change in the ratio of one isotope to another is not proportional to the difference in masses



$\Delta^{17}\text{O}$ as an Oxygen Source Tracer

Cap Delta, Δ ⁴

- $\Delta^{17}\text{O} = \delta^{17}\text{O} - (0.528)\delta^{18}\text{O}$



Slide 8

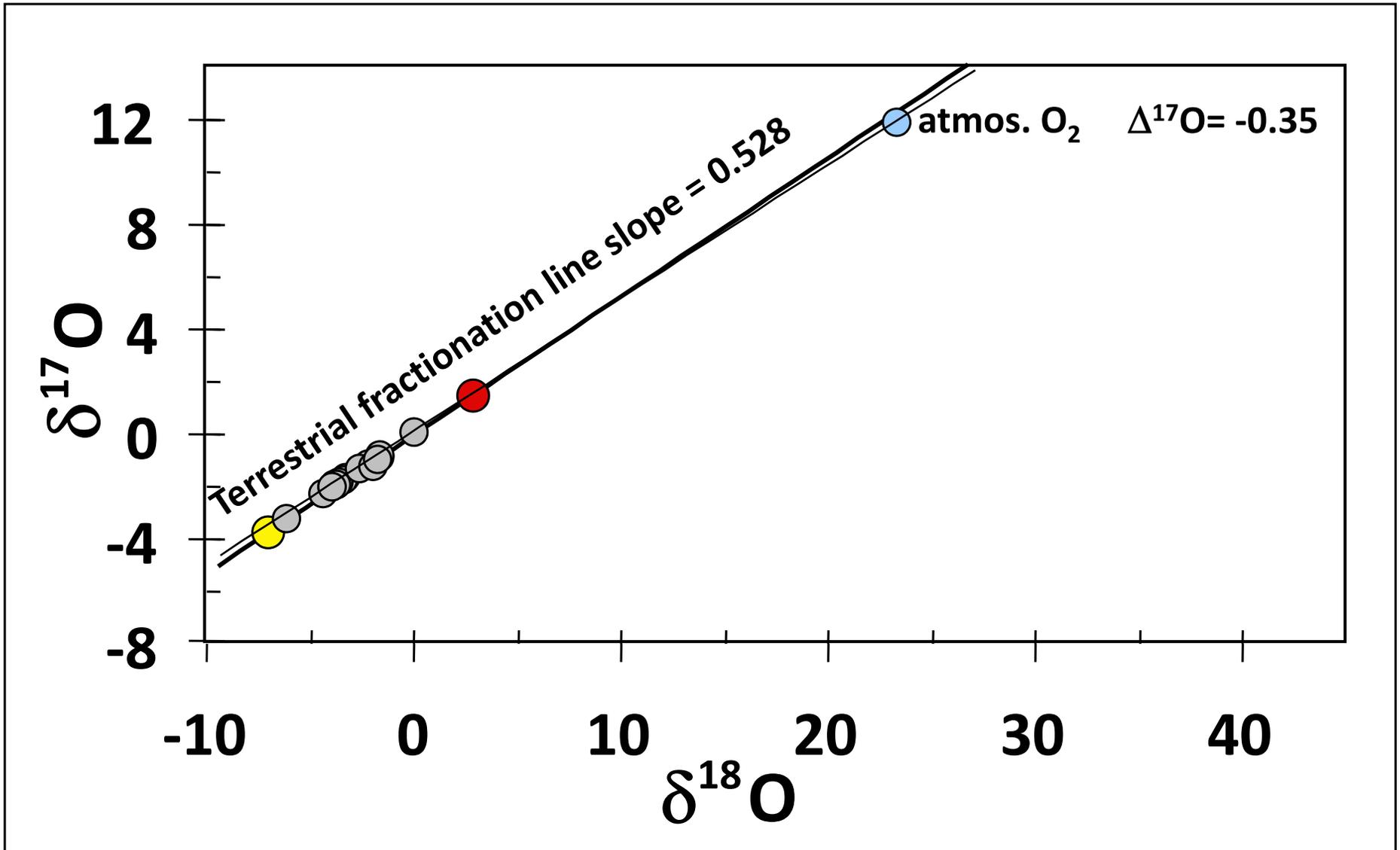
4

Added , after Cap Delta

Max Coleman, 11/16/2011

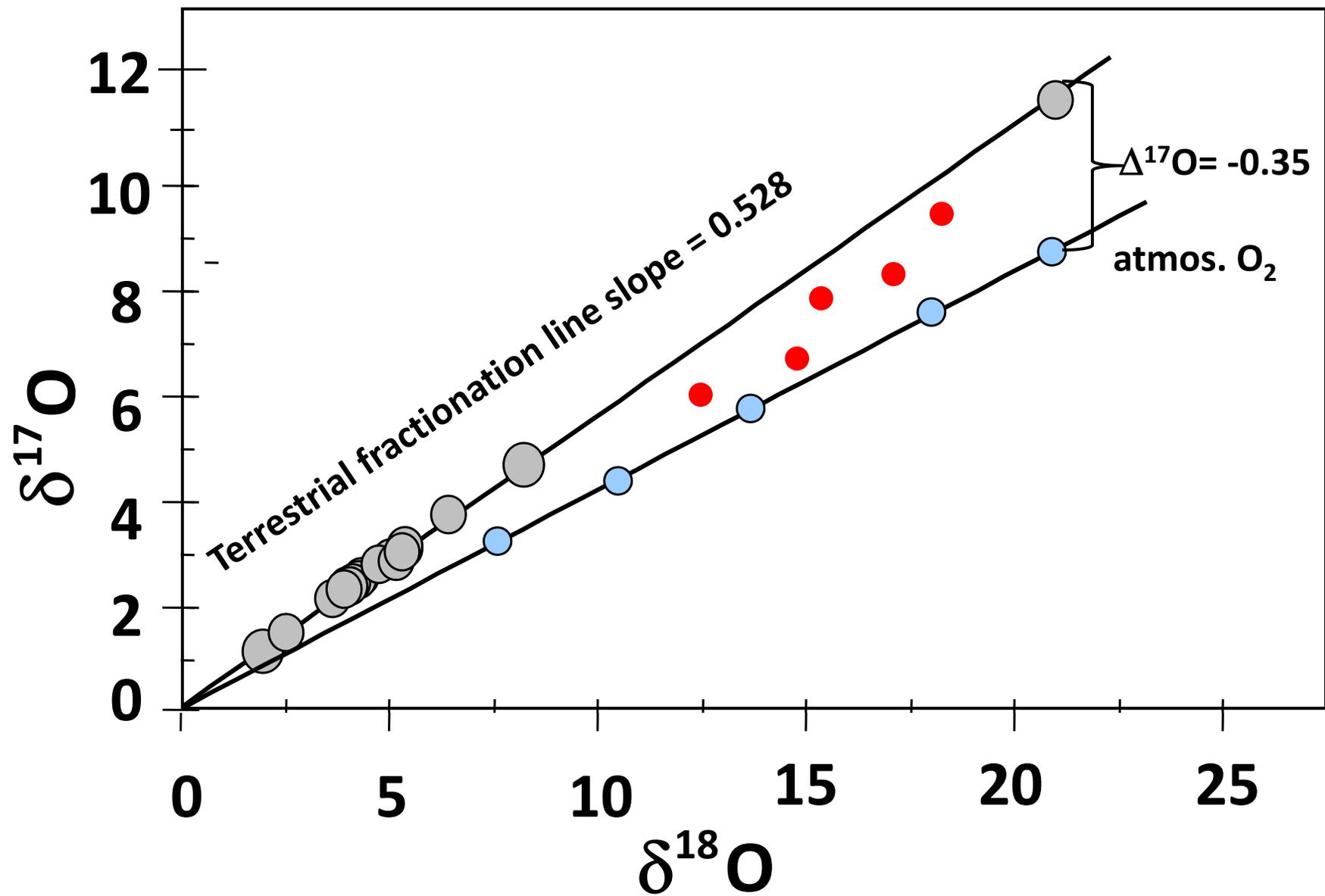


TFL and O₂





TFL and O₂





Methods

How to prepare samples and measure oxygen isotopes

- Precipitate sulfate in the form of BaSO_4 by the dropwise addition of BaCl_2
- DTPA dissolution and reprecipitation procedure (DDARP – Bao, 2006⁵)
- Wash 3 times in 18-M Ω water
- Dry for 24 hours at 100°C

Slide 11

5

made reference black font

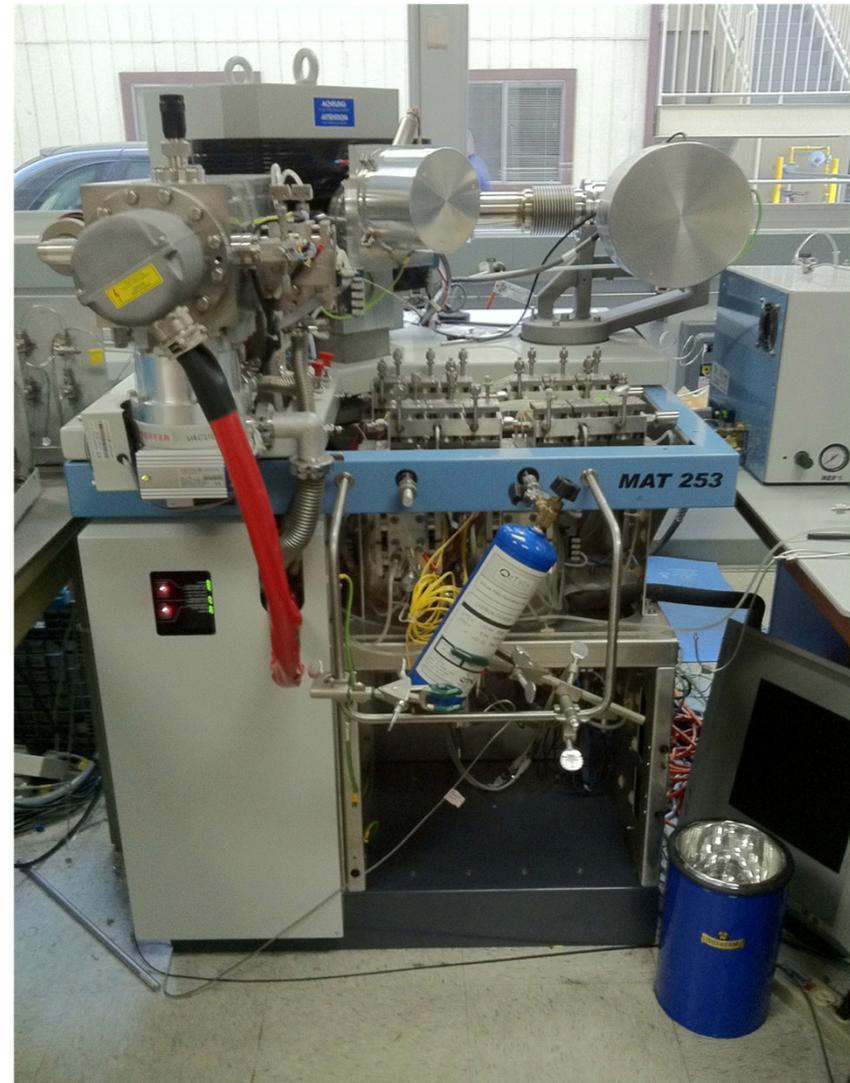
Max Coleman, 11/16/2011



$\Delta^{17}\text{O}$ Analysis

Laser Fluorination Line & Mass Spectrometer 6

- 30W CO₂ Laser
- LN₂ cold traps
- Molecular sieve
- Mass Spec



Slide 12

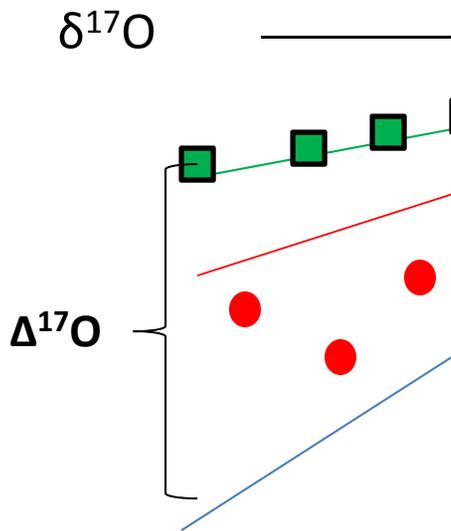
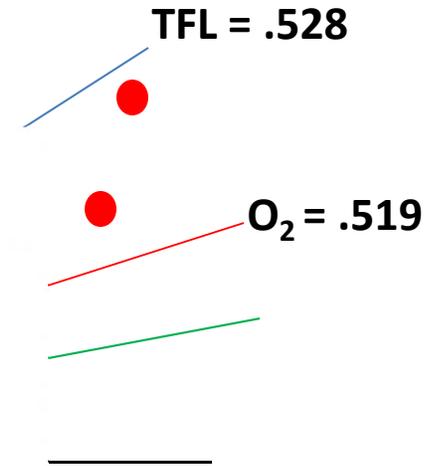
6

Added & Mass Spectrometer because it looked like the LFL was the title of the picture

Max Coleman, 11/16/2011



$\Delta^{17}\text{O}$ values range
from +0.070 to +0.183



$\delta^{18}\text{O}$

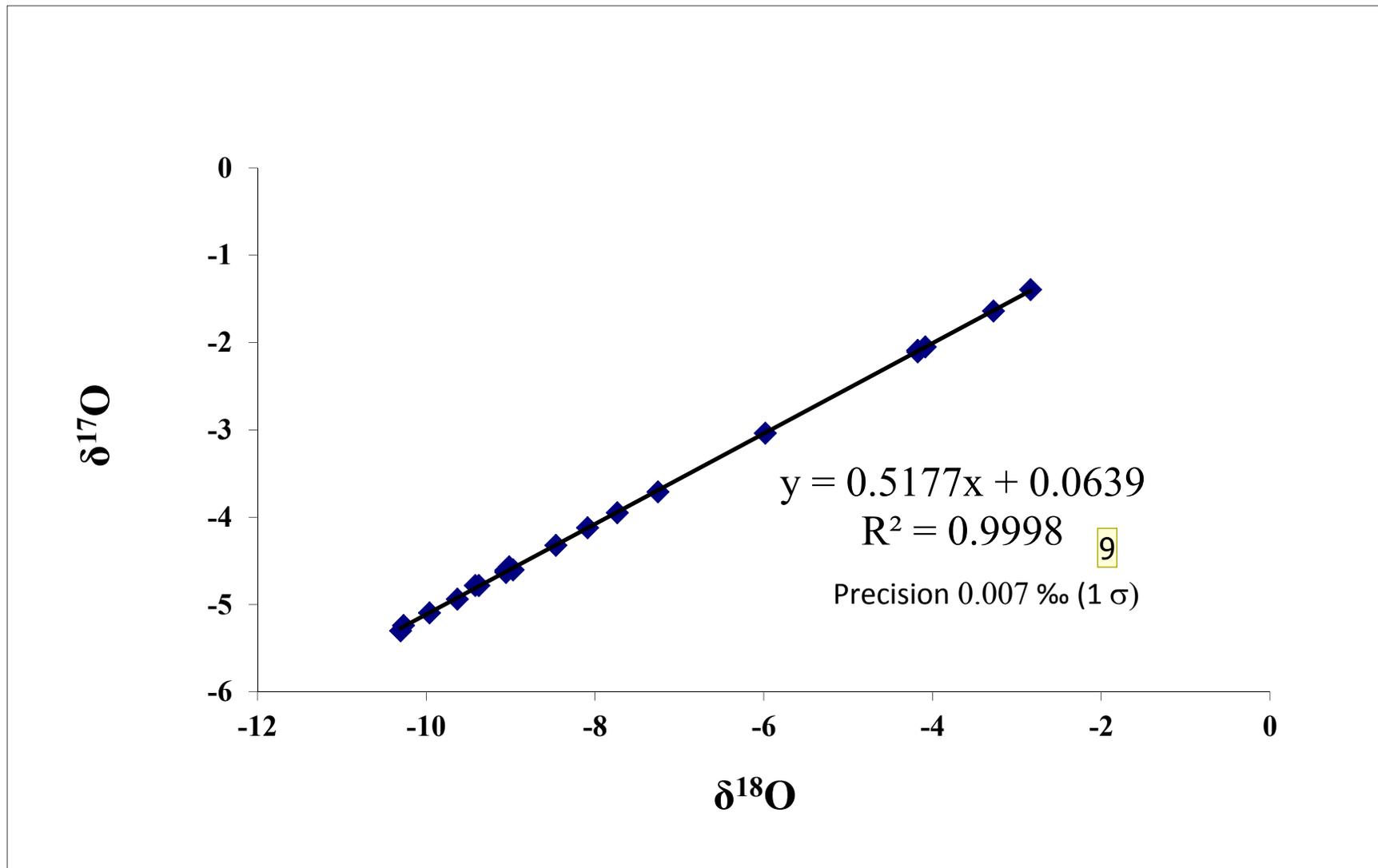
7

Made 17 and 18 superscript

Max Coleman, 11/16/2011



Rio Tinto SO₄ Results



Slide 14

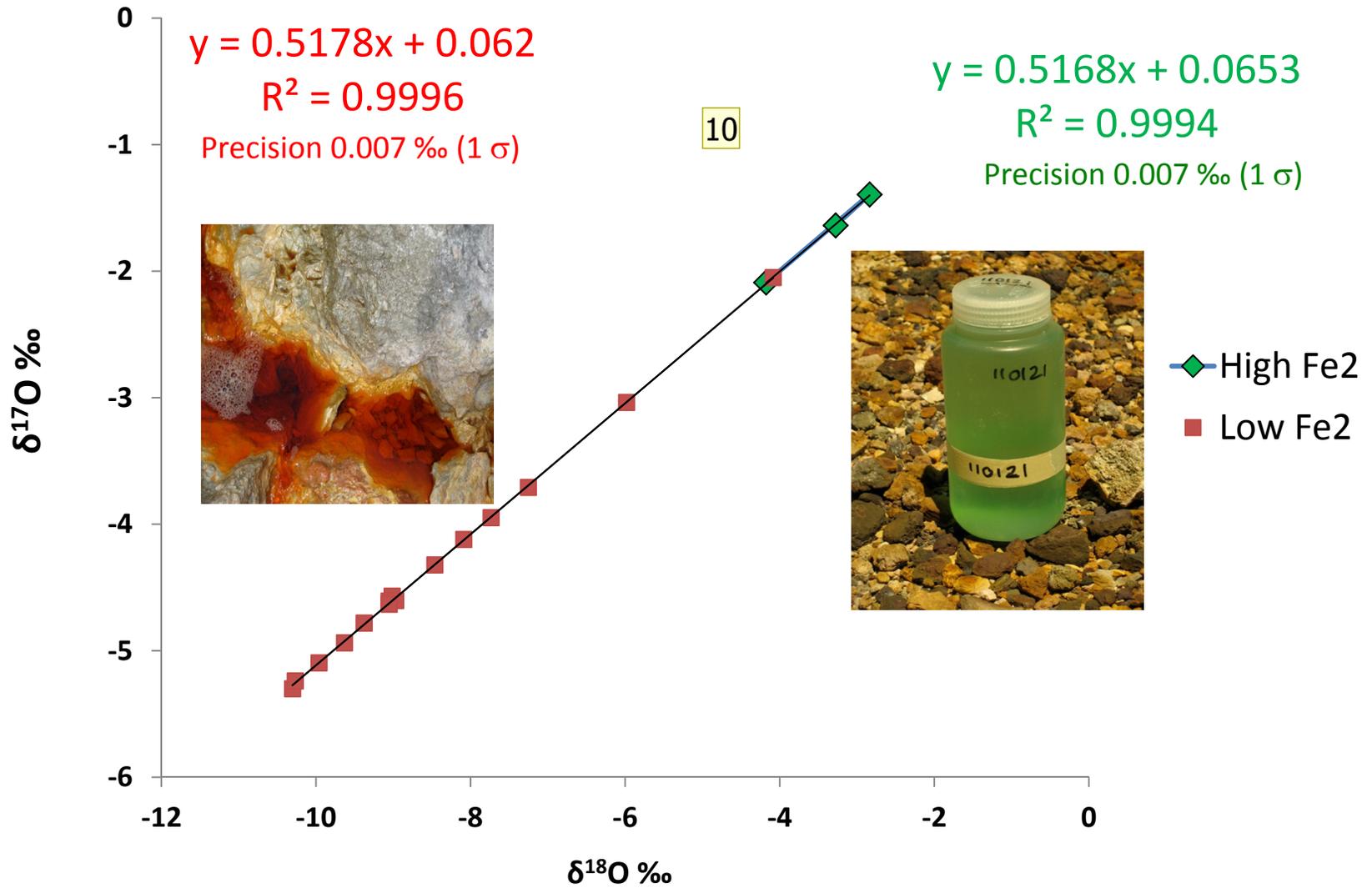
9

Changed reproducibility to precision and added 1 sigma

Max Coleman, 11/16/2011



Río Tinto SO₄



Slide 15

10

Changed reproducibility to precision and added 1 sigma twice

Max Coleman, 11/16/2011



Discussion



- May have new slope specific to sulfate production via oxidation of pyrite
- Strong correlation of data points suggest a dominant process for slope deviation
- Future work could determine microbe specific contribution to slope deviation



Conclusion

- Pyrite oxidation process specific slope does not allow for us to use $\Delta^{17}\text{O}$ as oxygen source tracer
- Process-specific contributions to slope deviation may lead to a new and novel biomarker
- $\delta^{18}\text{O}$ data show different oxidation pathways occurring but further work is needed to determine primary oxidant and fractionation factors



Acknowledgments

- This work was carried out at the Jet Propulsion Laboratory (JPL), California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA), supported by the NASA Astrobiology Institute (NAI)
- Max Coleman
- Issaku Kohl
- Randy Mielke
- Caltech SURF Program 11

Slide 18

11

Aded Caltech and Program - is it worth spelling out?

Max Coleman, 11/16/2011