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

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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
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

1. \( \text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \)

2. \( \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \)

**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
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 $\delta, \Delta$

• $\delta^{18}\text{O} = (R_{\text{Sample}}/R_{\text{Standard}} - 1)1000$

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

**Cap Delta, $\Delta$**

- $$\Delta^{17}O = \delta^{17}O - (0.528)\delta^{18}O$$
Added, after Cap Delta
Max Coleman, 11/16/2011
TFL and $O_2$

Terrestrial fractionation line slope = 0.528

$\delta^{17}O$ vs $\delta^{18}O$

atmos. $O_2$  $\Delta^{17}O = -0.35$
TFL and $O_2$

$\Delta^{17}O = -0.35$

Terrestrial fractionation line slope = 0.528

atmos. $O_2$
Methods
How to prepare samples and measure oxygen isotopes

• Precipitate sulfate in the form of $\text{BaSO}_4$ by the dropwise addition of $\text{BaCl}_2$
• DTPA dissolution and reprecipitation procedure (DDARP – Bao, 2006)
• Wash 3 times in 18-$\Omega$ water
• Dry for 24 hours at 100°C
made reference black font
Max Coleman, 11/16/2011
Δ$^{17}$O Analysis

Laser Fluorination Line & Mass Spectrometer

- 30W CO$_2$ Laser
- LN$_2$ cold traps
- Molecular sieve
- Mass Spec
Added & Mass Spectrometer because it looked like the LFL was the title of the picture
Max Coleman, 11/16/2011
$\Delta^{17}O$ values range from $+0.070$ to $+0.183$
Made 17 and 18 superscript
Max Coleman, 11/16/2011
Rio Tinto $SO_4$ Results

\[ y = 0.5177x + 0.0639 \]
\[ R^2 = 0.9998 \]

Precision 0.007 $\%_\sigma$ (1 $\sigma$)
9  Changed reproducibility to precision and added 1 sigma
Max Coleman, 11/16/2011
\[ y = 0.5178x + 0.062 \]
\[ R^2 = 0.9996 \]
Precision 0.007 ‰ (1 σ)

\[ y = 0.5168x + 0.0653 \]
\[ R^2 = 0.9994 \]
Precision 0.007 ‰ (1 σ)
Changed reproducibility to precision and added 1 sigma twice
Max Coleman, 11/16/2011
Discussion

$\Delta^{17}O$

- 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 $\Delta^{17}O$ as oxygen source tracer
• Process-specific contributions to slope deviation may lead to a new and novel biomarker
• $\delta^{18}O$ data show different oxidation pathways occurring but further work is needed to determine primary oxidant and fractionation factors
Acknowledgments

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• Max Coleman
• Issaku Kohl
• Randy Mielke
• Caltech SURF Program
Aded Caltech and Program - is it worth spelling out?
Max Coleman, 11/16/2011