Coupled C-S-Fe isotope variations in Archean-Paleoproterozoic shales trace microbial metabolisms and redox state in the early Earth

K.E. YAMAGUCHI[1,2], C.M. JOHNSON[2,3],
B.L. BEARD[2,3], S.R. POULSON[2,4], AND H. OHMOTO[2,5]

[1]IFREE,-JAMSTEC, Japan, (kosei@jamstec.go.jp)
[2]NASA Astrobiology Institute
[3]Dept. Geol. & Geophys., Univ. Wisconsin-Madison, USA,
[4]Dept. Geological Sciences, Univ. Nevada - Reno, USA
[5]Dept. Geosciences, The Pennsylvania State Univ., USA

Systematic variations among C_{org}, S, and Fe isotope and elemental compositions in 89 low-metamorphic grade drillcore samples of fine-grained Archean-Paleoproterozoic sedimentary rocks (Kaapvaal and Pilbara cratons) constrain microbial metabolisms and redox state between ~3.3 and ~2.2 Ga. Mineralogical and chemical compositions vary greatly: Fe (1~35 wt.% as total Fe), S (0~4 wt.%), and C_{org} (0~12 wt.%). C_{org}-rich rocks have strongly negative and variable δ^{56}Fe values (-2.3 to +0.6‰), where the most negative δ^{56}Fe values are restricted to samples where $\delta^{13}C_{org} < -35$, down to -50‰, suggesting that Fe^{3+} reduction may have been driven by methanogens in these samples. δ^{34}S and δ^{56}Fe values for these samples are negatively correlated, where δ^{34}S values as high as +15‰ suggest bacterial sulfate reduction under sulfate-limited conditions, consistent with an important role for methanogenesis. The negative δ^{56}Fe values, however, indicate that reactive Fe^{3+} was not limited. These relations provide powerful evidence that low-δ^{56}Fe Archean sedimentary rocks do not owe their origin to a low-δ^{56}Fe Archean ocean via extensive precipitation of oxides, as has been proposed, but instead reflect major biogeochemical cycling processes.

In contrast, S- and C_{org}-poor samples have restricted δ^{56}Fe values (-0.6 to +0.2‰), higher $\delta^{13}C_{org}$ values (-35 to -25‰), and modestly positive δ^{34}S values (0 to +5‰). The Fe budget in these samples is dominated by detrital components, and C_{org} and S isotope compositions record a component of photosynthesis and bacterial sulfate reduction, respectively. Some of these rocks have high Fe^{3+}/Fe^{2+} ratios, suggesting significant oxidation at ~3 Ga.

Collectively, these results provide evidence for a diverse biosphere in the Archean that involved a consortium of microbial communities that included cyanobacteria, sulfate-reducing bacteria, and methanogens/ methanotrophs; bacterial Fe^{3+} reduction may have been driven by dissimilatory iron reducing bacteria, sulfate-reducing bacteria, methanogens/ methanotrophs, or a combination of these, The significant inventory of Archean sedimentary rocks that have highly variable C_{org}, S, and Fe isotope compositions indicates that extensive microbially-mediated redox cycling of Fe, S, and C_{org} occurred in the Archean-Paleoproterozoic oceans. The Archean oceans could have been at least temporally, locally, and slightly oxygenated in order to form and retain sulfate and reactive Fe^{3+}. Therefore the oceans between ~3.3 and 2.2 Ga must have been, to some degree, stratified in redox state.

In situ isotope analysis of Fe in pyrite using laser ablation-ICPMS

HIROKI YAMAMOTO AND TAKAFUMI HIRATA

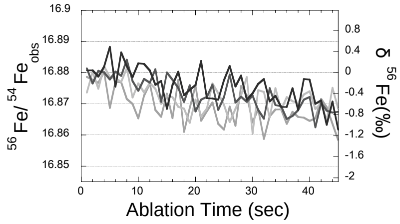
Laboratory for Planetary Sciences, Department of Earth and Planetary Sciences, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8551 (hiroki-y@geo.titech.ac.jp)

Introduction

Iron isotope provides us various key information about how the oxidative-reductive circumstance of the very dawn time was. Pyrite (FeS_2) is the most important mineral in sediments because of several unique features such as chemical robustness through mechanical transmutation or secondary metamorphic events. In order to derive precise and reliable Fe isotopic data from pyrite, recently developed laser ablation-ICP-mass spectrometry (LA-ICPMS) has been widely employed (Horn *et al*., 2006). However, in-situ isotopic analysis of Fe from pyrite using the LA-ICPMS technique has been retarded mainly because of poor analytical sensitivity and repeatability of the isotopic ratio measurements. It is widely recognised that the deterioration in analytical sensitivity and precision can be attributed to redeposition of sample around the laser ablation pit, and the measured isotope ratios (e.g., $^{56}Fe/^{54}Fe$) changed through ablation time (Jackson and Guenther, 2006, Hirata *et al*., 2005). In order to improve the reliability and precision of the Fe isotopic ratio measurements, resulting precision and accuracy of the $^{56}Fe/^{54}Fe$ ratio data obtained by the LA-ICPMS technique were rigorously tested.

Method

The graph below illustrates the changes in measured $^{56}Fe/^{54}Fe$ ratio against ablation time obtained by laser ablation of pyrite sample, demonstrating the isotopic fractionation (ca. 1‰ level) through laser ablation.



Series of experiments revealed that mass bias factor on $^{56}Fe/^{56}Fe$ ratio measurement was seriously dependent upon the amount of sample re-deposition around the ablation pit. In this paper, we will discribe the new approach to minimize the the isotopic fractionation using a femto-second laser ablation system.

References

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