様　式　C－１９、F－１９、Z－１９　（共通）

科研費
KAKENHI

科学研究費助成事業　　研究成果報告書

平成 ２７ 年　 ６ 月 ２２ 日現在

機関番号：３２６６１
研究種目：挑戦的萌芽研究
研究期間：2012～2014
課題番号：２４６５４１６４

研究課題名（和文）ラテライト形成過程と表層環境の地球史進化：鉄・三種酸素同位体の地球化学からの視点

研究課題名（英文）Iron and Oxygen Isotope Geochemistry of Lateritic Paleoweathering Profile in the Paleoproterozoic

研究代表者
山口　耕生（YAMAGUCHI, Kosei）

東邦大学・理学部・准教授

研究者番号：００３５９２０９

交付決定額（研究期間全体）：（直接経費）　　3,000,000円

研究成果の概要（和文）：約22億年前のラテライトの風化断面の鉄と酸素の安定同位体の地球化学より当時の大気中酸素濃度の程度を明らかにしようとする本研究では、鉄同位体比対酸素同位体比の負相関（ラテライト化作用が強い部位ほど54Feが溶脱して56Feにより富み、降水の影響下で形成する２次鉱物は18Oに枯渇する）を発見した。
数値モデル計算より、水／岩石比 が 10,000-100,000程度であり、現代のラテライトの形成時のものと同程度であること、ラテライト形成場は現代の（亜)熱帯域に相当したこと、さらに約22億年前の海洋の酸素同位体組成が 0 ‰であったことも示した。

研究成果の概要（英文）：Based on the iron and oxygen isotope compositions of Paleoproterozoic lateritic weathering profile discovered in Botswana (Yamaguchi et al., 2007; EPSL), a significant negative correlation between iron and oxygen isotope compositions (the more severe/advanced the lateritization was, the more enriched in heavy iron isotope and the more depleted in heavy oxygen isotope the profile has) was discovered for the first time. Then, a numerical calculation suggests that the water-rock ratios for such lateritization would have been around 10,000~100,000 (similar to modern values), lateritization occurred in (sub)tropical environment in the past, and the oxygen isotope composition of seawater 2.2 billion years ago was 0 per mil.

研究分野：アストロバイオロジー

キーワード：ラテライト　鉄　酸素　原生代

１．研究開始当初の背景

ラテライトの形成には雨季乾季の繰返しや超塩基性原岩等の条件が必要となり、主に熱帯地域に分布する。形成時に高い大気中酸素濃度が必要となるラテライトは、地球史初期には形成しなかった。南部アフリカに産する約 22 億年前の Hekpoort Basalt に発達したものが最古である。ボツワナの陸上掘削によるこの風化断面の発見前は、断面中位の鉄溶脱層より下の部位が、還元的大気下での形成故に表層から鉄が溶脱した古土壌の典型的断面とされてきた。このような層序の誤認によって、当時の大気の酸素濃度が極めて低かったとされた（Holland, 1994）

最古のラテライトの形成メカニズムを解明する事は、鉱床成因論のみならず大気進化史の制約に関して非常に重要である。しかしながら、先カンブリア時代のラテライトの形成プロセスに関する地球化学的研究は、国内外とも皆無に近い。唯一の例が、研究代表者らが出版した論文（Yamaguchi *et al.* 2007; EPSL）である。

２．研究の目的

大気中酸素濃度の急上昇期とされる約 22 億年前に発達した世界最古のラテライト質風化断面を主な研究対象に設定して、鉄酸化物の鉄–酸素の安定同位体地球化学を展開し、ラテライトの鉄–酸素の安定同位体地球化学のレファレンスとなるデータセット構築を行う。形成場における水–岩石の相互作用・古緯度・海水の酸素同位体組成等の推定を行い、ラテライト形成の定量的モデル構築を行うと同時に地球史初期の表層環境進化を探り、地球表層環境の進化に関する重要な知見を得ることが目的である。

３．研究の方法

約 22 億年前のラテライト質風化断面の試料を用いて、鉄酸化物の鉄–酸素の安定同位体地球化学組成を測定する。マスバランス計算等の手法から、形成場における水–岩石の相互作用・大気中の光化学反応の痕跡・古緯度・海水の酸素同位体組成等の推定を行う。

４．研究成果

約 22 億年前のラテライトの風化断面において、鉄同位体比対酸素同位体比の負相関を発見した。つまり、水―岩石相互作用、すなわちラテライト化作用が強い部位ほど ^{54}Fe が溶脱して ^{56}Fe により富み、降水の影響下で形成する２次鉱物は ^{18}O に枯渇する、ことを示唆する。

数値モデル計算より、ラテライトの形成時の水/岩石比は 10,000～100,000 程度であったことがわかった。この水/岩石比の範囲は、現代のラテライトの形成時のものと同程度であること、ラテライト形成場は現代の（亜)熱帯域に相当したこと、さらに約 22 億年前の海洋の酸素同位体組成が 0 ‰ であったことも示した。最後に、現世のラテライト形成過程と同様に、鉄の溶脱過程において陸上生命活動を起源とする有機酸が、太古のラテライト形成においても重要であった可能性が示唆できた。本研究成果は、初期地球における微生物生命圏、特に陸上における微生物生命圏の発達に関して重要な示唆を持つ。

５．主な発表論文等

〔雑誌論文〕（計 4 件）

1. Barlow, E., Van Kranendonk, M.J., <u>Yamaguchi, K.E.</u>, Hegner, E., Yamada, K., Ikehara, M., and Lepland, A. (2015) Life’s adaptation to the oxygen revolution: Litho-stratigraphic analysis of a stromatolite-thrombolite reef from the Paleoproterozoic Turee Creek Group, Western Australia. Geobiology, in press. ［査読有］
2. Van Kranendonk, M.J., Mazumder, R., <u>Yamaguchi, K.E.</u>, Yamada, K., and Ikehara, M. (2015) Sedimentology of the Paleoproterozoic Kungarra Formation, Turee Creek Group, Western Australia: A conformable record of the transition from early to modern Earth. Precambrian Research 256, 314-343. ［査読有］
3. Czaja, A.D., Johnson, C.M., <u>Yamaguchi, K.E.</u>, and Beard, B.L. (2012) Comments on “Abiotic pyrite formation produces a large Fe isotope fractionation. Science 335, 538. ［査読有］
4. Kiyokawa, S., Takashi, I., Ikehara, M., <u>Yamaguchi, K.E.</u>, Koge, S., and Sakamoto, R. (2012b) Lateral variations in the lithology and organic chemistry of a black shale succession of the Mesoarchean Dixon Island Formation in the coastal Pilbara Terrane, Western Australia: Influence by syndepositional hydrothermal activity. Island Arc 21, 118–147. ［査読有］

〔学会発表〕（計 39 件）

1. <u>Yamaguchi, K.E.</u>, Naraoka, N., Ikehara, M., Ito, T., and Kiyokawa, S. (2014b) Biogeochemical cycling of Fe, S, C, N, and Mo in the 3.2 Ga ocean: Constraints from DXCL-DP black shales from Pilbara, Western Australia. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 15-19. Abstract.
2. Minami, H., Abe, A., <u>Yamaguchi, K.E.</u>, and Naraoka, N. (2014) Sulfur speciation and isotope analysis of the 2.7 Ga shallow-

and deep-facies black shales from Pilbara, Western Australia. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 15-19. Abstract.
3. Tomiuka, T. and Yamaguchi, K.E. (2014) Geochemistry of carbon and sulfur in the 2.7 Ga stromatolitic carbonate and shale (ABDP#10 core) from Meentheena, Western Australia. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 15-19. Abstract.
4. Miki, T., Kiyokawa, S., Ito, T., Ikehara, M., Yamaguchi, K.E. (2014b) Organic / inorganic carbon content and isotope analysis of 3.1Ga Cleaverville Formation in Pilbara, Australia: Result of DXCL project. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 15-19. Abstract.
5. Kiyokawa, S., Ito, T., Ikehara, M., Yamaguchi, K.E., Naraoka, H., Onoue, T., Horie, K., Aihara, Y., Miki, T. (2014) Mesoarchean oceanic floor environment at sedimentary sequences in Dixon Island-Cleaverville Formation formations, Pilbara Australia: Result of DXCL drilling project. In 21st General Meeting of the International Mineralogical Association, Sandton City, South Africa, Sep. 1-5.
6. Miki, T., Kiyokawa, S., Naraoka, H., Takahata, N., Ishida, A., Ito, T., Ikehara, M., Yamaguchi, K.E., Sakamoto, R., and Sano, Y. (2014a) Reconstruction of 3.2Ga sea floor environment: In situ and whole-rock analysis of carbon and sulfur isotope of DXCL project. In 21st General Meeting of the International Mineralogical Association, Sandton City, South Africa, Sep. 1-5.
7. Yamaguchi, K.E., Kobayashi, Y. Shiina, A., Yamada, K., Kobayashi, D., Nakamura, T., Sakamoto, R., Naraoka, H., Ikehara, M., Ito, T., and Kiyokawa, S. (2014a) Oxidative biogeochemical cycling of Fe, S, C, N, and Mo in the 3.2 Ga ocean: Constraints from DXCL-DP sulfidic black shales from northwestern Pilbara, Western Australia. In Origins 2014, 2nd ISSOL – The International Astrobiology Society and Bioastronomy (IAU C51), Joint International Conference, Nara, Japan, July 6-11.
8. Minami, H., Abe, A., Yamaguchi, K.E., Naraoka, H. (2014a) Sulfur speciation and isotope analysis ofin the 2.7 Ga shallow- and deep-facies black shales from Pilbara, Western Australia. In Origins 2014, 2nd ISSOL – The International Astrobiology Society and Bioastronomy (IAU C51), Joint International Conference, 奈良市公会堂（奈良県奈良市）, July 6-11.
9. Nakamura, T., Yamaguchi, K.E., Ikehara, M., Kiyokawa, S., and Ito, T. (2014a) Origin of organic matter in 3.2 Ga black shales revealed by infrared and laser Raman microspectroscopy. In Origins 2014, 2nd ISSOL – The International Astrobiology Society and Bioastronomy (IAU C51), Joint International Conference, 奈良市公会堂(奈良県奈良市), July 6-11.
10. Tomiuka, T., Yamaguchi, K.E., Sakai, S. (2014a) Geochemistry of C, O and S in the 2.7 Ga stromatolite (ABDP#10 core) from Meenthena, Western Australia. In Origins 2014, 2nd ISSOL – The International Astrobiology Society and Bioastronomy (IAU C51), Joint International Conference, 奈良市公会堂(奈良県奈良市), July 6-11.
11. Kotani, M., Yamaguchi, K.E., and Ikehara, M. (2014a) Denitrification in the Mesoarchean deep ocean: Evidence from nitrogen isotope compositions of kerogen in black shales from Pilbara, Western Australia. In Origins 2014, 2nd ISSOL – The International Astrobiology Society and Bioastronomy (IAU C51), Joint International Conference, 奈良市公会堂（奈良県奈良市）, July 6-11.
12. Shiina, A., Yamaguchi, K.E., Kiyokawa, S., Ikehara, M., and Ito, T. (2014a) Constraints for oceanic redox conditions from Fe speciation analysis of 3.2 Ga DXCL-DP black shales, Cleaverville Group, Western Australia. In Origins 2014, 2nd ISSOL – The International Astrobiology Society and Bioastronomy (IAU C51), Joint International Conference, 奈良市公会堂（奈良県奈良市）, July 6-11.
13. Kiyokawa, S., Ito, T., Ikehara, M., Yamaguchi, K.E., Naraoka, H., Onoue, T., Horie, K., Sakamoto, R., Aihara, Y., and Miki, T. (2013b) Mesoarchean Banded Iron Formation sequences in Dixon Island-Cleaverville Formation, Pilbara Astralia: Oxygenic signal from DXCL project. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 9-13.
14. Aihara, Y., Kiyokawa, S., Ito, T., Ikehara, M., Yamaguchi, K.E., Horie, K., Sakamoto, R., and Miki, T. (2013) Field occurrence and lithology of Archean hydrothermal systems in the 3.2 Ga Dixon Island Formation, Western Australia. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 9-13. Abstract.
15. Miki, T., Kiyokawa, S., Takahata, N.,

Ishida, A., Ito, T., Ikehara, M., Yamaguchi, K.E., Sakamoto, R., and Sano, Y. (2013b) Heterogeneity of S isotope ratios of Mesoarchean minute spherical pyrite crystals: NanoSIMS analysis for the 3.2Ga black shale from DXCL Drilling Project in Pilbara, Australia. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 9-13.

16. Yamaguchi, K.E. and Abe, A. (2013) Geochemical evidence for redox stratification of the ocean 2.7 billion years ago. In International Biogeoscience Conference, 名古屋大学（愛知県名古屋市）, Nov. 1-4.
17. Kiyokawa, S., Ito, T., Ikehara, M., Yamaguchi, K.E., Naraoka, H., Onoue, T., Horie, K., Sakamoto, R., Aihara, Y., and Miki, T. (2013a) Oceanic sedimentary sequences in Mesoarchean Dixon Island-Cleaverville Formation, Pilbara Australia: Result of DXCL drilling project. In International Biogeoscience Conference, 名古屋大学(愛知県名古屋市), Nov. 1-4.
18. Aihara, Y., Kiyokawa, S., Ito, T., Ikehara, M., Yamaguchi, K.E., Horie, K., Sakamoto, R., and Miki, T. (2013a) Field occurrence and lithology of Archean hydrothermal systems in the 3.2 Ga Dixon Island Formation, Western Australia. In International Biogeoscience Conference, 名古屋大学(愛知県名古屋市), Nov. 1-4.
19. Miki, T., Kiyokawa, S., Takahata, N., Ishida, A., Ito, T., Ikehara, M., Yamaguchi, K.E., Sakamoto, R., and Sano, Y. (2013a) Heterogeneity of sulfur isotope compositins of spherical pyrite revealed by NanoSIMS analysis of the 3.2 Ga black shale from DXCL Drilling Project in Pilbara, Australia.. In International Biogeoscience Conference, 名古屋大学（愛知県名古屋市）, Nov. 1-4.
20. Minami, H., Abe, A., Naraoka, H., and Yamaguchi, K.E (2013b) Redox stratification of the ocean 2.7 billion years ago:Constraints from speciation analysis of sulfur and iron in the shallow- and deep-facies black shales from Pilbara, Western Australia. In International Biogeoscience Conference, 名古屋大学（愛知県名古屋市）, Nov. 1-4.
21. Nakamura, T., Yamaguchi, K.E., Ikehara, M., Kiyokawa, S. and Ito, T. (2013) Origin of organic matter in 3.2 Ga black shales revealed by infrared and laser Raman microspectroscopy. In International Biogeoscience Conference, 名古屋大学（愛知県名古屋市）, Nov. 1-4.
22. Shiina, A., Yamaguchi, K.E., Kiyokawa, S., Ikehara, M., and Ito, T. (2013) Constraints for oceanic redox conditions from Fe speciation analysis of 3.2 Ga DXCL-DP black shales, Cleaverville Group, Western Australia. In International Biogeoscience Conference, 名古屋大学（愛知県名古屋市）, Nov. 1-4.
23. Yahagi, T.R., Yamaguchi, K.E., Haraguchi, S., Sano, R., Teraji, S., Kiyokawa, S., Ikehara, M., Ito, T. (2013b) REE and Oxygen Isotope Geochemistry of ~3.2 Ga BIFs: Comparison between Barberton, South Africa and Pilbara, Western Australia. In International Biogeoscience Conference, 名古屋大学（愛知県名古屋市）, Nov. 1-4.
24. Yamaguchi, K.E., Kobayashi, D., Yamada, K., Sakamoto, R., Hosoi, H., Kiyokawa, S., Ikehara, M., Ito, T. (2013c) Biogeochemical cycling of nitrogen and carbon in the 3.2 Ga ocean: Results from DXCL-DP, NW Pilbara, Western Australia. In 23rd V.M. Goldschmidt Conference, Florence, Italy, Aug. 25-30.
25. Yahagi, T.R., Yamaguchi, K.E., Haraguchi, S., Sano, R., Teraji, S., Kiyokawa, S., Ikehara, M., Ito, T. (2013a) REE Geochemistry of ~3.2 Ga old BIFs from the Mapepe Formation and Msauli Member, Barberton, South Africa. In 23rd V.M. Goldschmidt Conference, Florence, Italy, Aug. 25-30.
26. Yamaguchi, K.E., Abe, A., Kobayashi, Y., Kobayashi, D., Nakamura, T., Ikehara, M., Haraguchi, S., Sakamoto, R., Naraoka, H., Kiyokawa, S., and Ito, T. (2013a) Geochemistry of C, N, S, Fe, and Mo in the 3.2 and 2.7 Ga sulfide-rich carbonaceous shales from Pilbara Craton, Western Australia. In Meeting of the Americas, Cancun, Mexico, May 14-17.
27. Yamaguchi, K.E., Abe, A., Kobayashi, Y., Kobayashi, D., Nakamura, T., Ikehara, M., Haraguchi, S., Sakamoto, R., Naraoka, H., Kiyokawa, S. and Ito, T. (2012e) Biogeochemistry of C, N, S, Fe, and Mo and origin of organic matter in the 3.2 and 2.7 Ga sulfidic black shales from Pilbara, Western Australia: A synthesis. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 3-7.
28. Abe, A., Yamaguchi, K.E., Haraguchi, S., Naraoka, H., Naito, K., and Yahagi, T.R. (2012) Redox stratification of the ocean 2.7 billion years ago: Preliminary results from Fe speciation analysis of shallow- and deep-facies black shales. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 3-7.
29. Kobayashi, Y., Yamaguchi, K.E.,

Sakamoto, R., Naraoka, H., Kiyokawa, S., Ikehara, M., and Ito, T. (2012) Marine sulfur cycle constrained from isotope analysis of different forms of sulfur in the 3.2 Ga black shale (DXCL-DP) from Pilbara, Australia. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 3-7.

30. Yahagi, T., Yamaguchi, K.E., Haraguchi, S., Sano, R., Teraji, S., Kiyokawa, S., Ikehara, M., and Ito, T. (2012) REE geochemistry of 3.2 Ga BIF from the Mapepe Formation, Barberton Greenstone Belt, South Africa. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 3-7.
31. Kiyokawa, S. Ito, T., Ikehara, M., Yamaguchi, K.E., Onoue, T., Horie, K., Sakamoto, R., Teraji, S., and Aihara, Y. (2012c) Mesoarchean black shale -iron sedimentary sequences in Cleaverville Formation, Pilbara Australia: drilling preliminary result of DXCL2. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 3-7.
32. Teraji, S., Kiyokawa, S., Ito, T., Yamaguchi, K.E., Ikehara, M., and Inamoto, Y. (2012c) 3.2 Ga ocean sedimentary sequence in the Komati section of the Mapepe Formation in the Barberton Greenstone Belt, South Africa. In American Geophysical Union, Fall Meeting, San Francisco, CA, USA, December 3-7.
33. Yamaguchi, K.E., Kobayashi, Y., Kobayashi, D., Nakamura, T., Ikehara, M., Sakamoto, R., Naraoka, H., Kiyokawa, S., and Ito, T. (2012d) Elemental cycling of C, N, P, S, Fe, and Mo and origin of organic matter in the 3.2 Ga old black shales recovered by DXCL-DP in Pilbara, Western Australia. In 34th International Geological Congress, Brisbane, Australia, Aug. 5-10.
34. Kiyokawa, S., Ito, T., Ikehara, M., Yamaguchi, K.E., Horie, K., Sakamoto, R., Takehara, M., and Aihara, Y. (2012b) Mesoarchean oceanic sedimentary sequences: DXCL1 and 2 drilling project. In 34th International Geological Congress, Brisbane, Australia, Aug. 5-10.
35. Teraji, S., Kiyokawa, S., Ito, T., Yamaguchi, K.E., Ikehara, M., and Inamoto, Y. (2012b) Relatively deep ocean sedimentary sequence in the Komati section of the 3.2 Ga Mapepe Formation in the Barberton Greenstone Belt, South Africa. In 34th International Geological Congress, Brisbane, Australia, Aug. 5-10.
36. Yamaguchi, K.E. (2012a) Biogeochemical cycling of carbon, nitrogen, sulfur and phosphorus recorded in the surface sediment of coastal and meromictic Lake Kai-ike, southwest Japan. In 50th ECSA (Estuarine and Coastal Science) Conference: Today's science for tomorrow's Management, Venice (Venezia), Italy, June 3-7.
37. Ohmoto, H., Watanabe, Y., Yamaguchi, K.E., Hamasaki, H., Brainard, J., and Chorney, A. (2012b) Evidence for the O2 and CO2 rich Archean atmosphere. In 22nd V.M. Goldschmidt Conference, Montreal, Canada, June 24-29.
38. Yamaguchi, K.E., Kobayashi, Y., Kobayashi, D., Nakamura, N., Sakamoto, R., Naraoka, H., Ikehara, M., Ito, T., and Kiyokawa, S. (2012b) Biogeochemical cycling of C, N, P, S, Fe, and Mo and origin of organic matter in the 3.2 Ga old black shales recovered by DXCL-DP in Pilbara, Western Australia. In Astrobiology Science Conference 2012, Atlanta, GA, USA, April 16-20.
39. Ohmoto, H., Watanabe, Y., Yamaguchi, K.E., Brainard, J., and Chorney, A. (2012a) Evidence in the isotopic records of C, N, S, Fe, Mo, Cr and Pb in Archean rocks for the early development of the fully-oxygenated atmosphere and oceans. In Astrobiology Science Conference 2012, Atlanta, GA, USA, April 16-20.

〔図書〕（計３件）

1. 山口 耕生 (2012c) 地球史と鉱床形成. In 地球と宇宙の化学辞典、1-07、 p. 9、朝倉書店.
2. 山口 耕生 (2012b) 古土壌と大気進化. In 地球と宇宙の化学辞典、1-19、 p. 25-27、朝倉書店.
3. 山口 耕生 (2012a) 大気中酸素濃度上昇. In 地球と宇宙の化学辞典、1-26、 p. 38-39、朝倉書店.

６．研究組織

(1)研究代表者

山口耕生（YAMAGUCHI, Kosei）
東邦大学・理学部・准教授
研究者番号：００３５９２０９

(2)研究分担者

なし

(3)連携研究者

なし