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Direct Evidence for Oxygenated Atmosphere More Than Three Hundred Million Years before the Great Oxidation Event (GOE) ~Great impact on the elucidation of co-evolutionary relationship between life and atmosphere~

Abstract

The research group of the Institute for Research on Earth Evolution (IFREE: Yoshio Fukao, Director) of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC: Yasuhiro Kato, President) and the University of Tokyo (Hiroshi Komiyama, President) has found direct evidence for the oldest oxygenated atmosphere ([*1](#)) on Earth from rock core samples obtained from the geoscientific drilling in Western Australia.

It has been generally believed that Earth's atmosphere was anoxic until 2.45 ~2.32 billion years ago. However, the hematized basalts ([*2](#)) formed through the reaction with oxygenated groundwater were discovered at deeper than 200m below the present land surface using diamond drilling, and age of pyrite ([*3](#)) veinlets cross-cutting the hematized basalts was successfully determined to be 2.76 billion years ago (Ga) using the Re-Os method ([*4](#)).

This result suggests that oxygenated atmosphere most likely emerged 300 million years earlier than previously thought.

As geoscientific information about surface environments and biospheric evolution on early Earth is very little, the present results directly constraining the contemporaneous surface environment are very important to understand global environmental changes. Because the occurrence of oxygenated atmosphere has a genetical linkage to the existence of oxygenic cyanobacteria, this finding reporting the emergence of oxygenated atmosphere more than 300 million years before the widely accepted GOE gives a great impact on research fields of the history of life.

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Title: Hematite formation by oxygenated groundwater more than 2.76 billion years ago

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Background

Timing of the emergence of oxygenated atmosphere is one of the most important turning points for the development and evolution of aerobic respiratory life on Earth, including human beings, and hence it has been one of the greatest scientific subjects.

Based on a series of studies on the mass independent fractionation ([*5](#)) of sulfur isotopes in sedimentary rocks, which stem from the scientific report published in 2000 by the research group of the University of California, San Diego, the currently accepted theory that an oxygenated atmosphere emerged 2.45 ~ 2.32 billion years ago (GOE, Great Oxidation Event) has been established.

However, it has been recently pointed out that other geochemical processes can also create mass independent fractionation of sulfur isotopes.

Study methods

The diamond drilling to a down-hole depth of 260 meters below the present land surface was carried out at Marble Bar in the Pilbara Craton, Western Australia in 2003 as an international scientific project, Archean Biosphere Drilling Project (ABDP) ([*6](#)), involving geologists from Japan, USA and Australia ([Fig.1](#)).

Hematized basalts were discovered in the core samples obtained from a depth of 210~235m ([Fig.2](#)). These are primarily submarine basalts ([Apex Basalt; *7](#)) that were erupted onto the Archean seafloor 3.46 billion years ago. Due to 2.9 Ga orogenic deformation and subsequent deep erosion, the Apex Basalt was exposed at the surface of a continental landmass prior to 2.77 billion years ago. After covering of continental flood-basalt ([*8](#)) more than three kilo meters in thickness, the Apex basalt was exposed to the surface again late in the Phanerozoic (since three hundred million years ago).

Hematized basalts occur along the bedding-parallel shear zone close to the contact with chert ([*9](#)) beds, and were very likely formed by the infiltration of oxygenated groundwater. Moreover, pyrite veinlets that cross-cut the hematized basalts are observable ([Fig.3](#)). The occurrence of pyrite clearly indicates that the pyrite formed after the hematize. Determination of the age of the pyrite formation by Re-Os method constrains the age of the hematization in turn. Therefore, twenty sample chips including pyrite veinlets were prepared for the age determination by Re-Os method.

Summary of result

The age determination by Re-Os method revealed that the pyrite veinlets were formed 2.763 billion years ago ([Fig.4](#)). The present results demonstrated that the hematization of basalt occurred prior to 2.763 billion years ago. Based on lines of evidence from local geology of the Marble Bar area, the hematization most likely formed by the reaction of basalts with O₂-rich groundwater sometime between 2.9 to 2.77 billion years ago.

The present measurements indicate that oxygenated atmosphere existed more than 300 million years earlier than widely believed. In addition, based on a mass-balance calculation for hematized and non-hematized basalts, the atmospheric oxygen level can be estimated to be 1.5 % of the present atmospheric value.

Future prospective

The present results greatly contribute to the establishment of the model of atmospheric evolution.

Furthermore, they give a great impact on the understanding of the history of life. To determine the timing of emergence of oxygenated atmosphere provides an important constraint on the evolution of aerobic respiratory life on Earth, and also gives a hint to resolving the reason why the aerobic respiratory life including human beings could evolve on Earth.

Further research is expected to unravel a close linkage between global environmental changes of early Earth and the development and evolution of life.

*1: oxygenated atmosphere

Atmosphere is regarded as "oxygenated" in the case of the oxygen level greater than 1/100,000 (0.0002%) of the present atmospheric level (PAL).

*2: hematite

Hematite is the mineral form of ferric(Fe^{3+}) oxide and often forms under an oxygenated environment. Fe_2O_3 .

*3: pyrite

Pyrite is the mineral form of ferrous (Fe^{2+}) sulfide and form through reactions between iron and sulfur. This mineral is often observed in sedimentary rocks or mineral deposits and is called as fool's gold due to its resemblance to gold. FeS_2 .

*4: Re-Os dating method

It is a dating method based on beta decay (decay emitting beta radiation) of $^{187}\text{Rhenium}$ (Re) with a 40 billion years half-life into $^{187}\text{Osmium}$. Radioisotope "Rhenium" (mother radionuclide) gradually changes to stable nuclide "Osmium" (daughter nuclide) while emitting radiation. Since a radioactive decay occurs at a uniform rate, the age can be determined if the quantity of decayed isotopes is precisely measured. Other dating techniques with a similar principle are uranium - lead dating for rock samples and C-14 dating for archaeological sites.

*5: mass independent isotope fractionation

Mass independent isotope fractionation refers to any chemical or physical process acting to separate isotopes, where the amount of separation is not proportioned with the difference in the masses of the isotopes. Mass independent fractionation of sulfur isotopes has been discovered from ancient geological samples more than 2.45 billion years ago. Although a detailed process of fractionation has not yet known, the most plausible is photochemical reactions involving sulfur-bearing molecules in the anoxic atmosphere. However, it has been recently reported that mass independent fractionation of sulfur isotopes can be created by other processes, and hence the relation between mass independent fractionation of sulfur isotopes and anoxic atmosphere remains unresolved.

*6: ABDP (Archean Biosphere Drilling Project)

The ABDP is the geoscientific drilling project at Pilbara, Western Australia, which commenced as the collaborating research of Japan, US and Australia in order to elucidate environmental changes of early Earth and the development of life.

*7: submarine basalt

Submarine basalt is an extrusive volcanic rock on seafloor.

*8: flood basalt

Flood basalt is an extrusive volcanic rock as a result of a giant volcanic eruption or series of eruptions that covers the large areas of land or ocean floor.

*9: chert

Chert is a fine-grained silica-rich microcrystalline or cryptocrystalline sedimentary rock sometimes containing microfossils.



Fig.1 Geoscientific drilling at Marble Bar in Western Australia

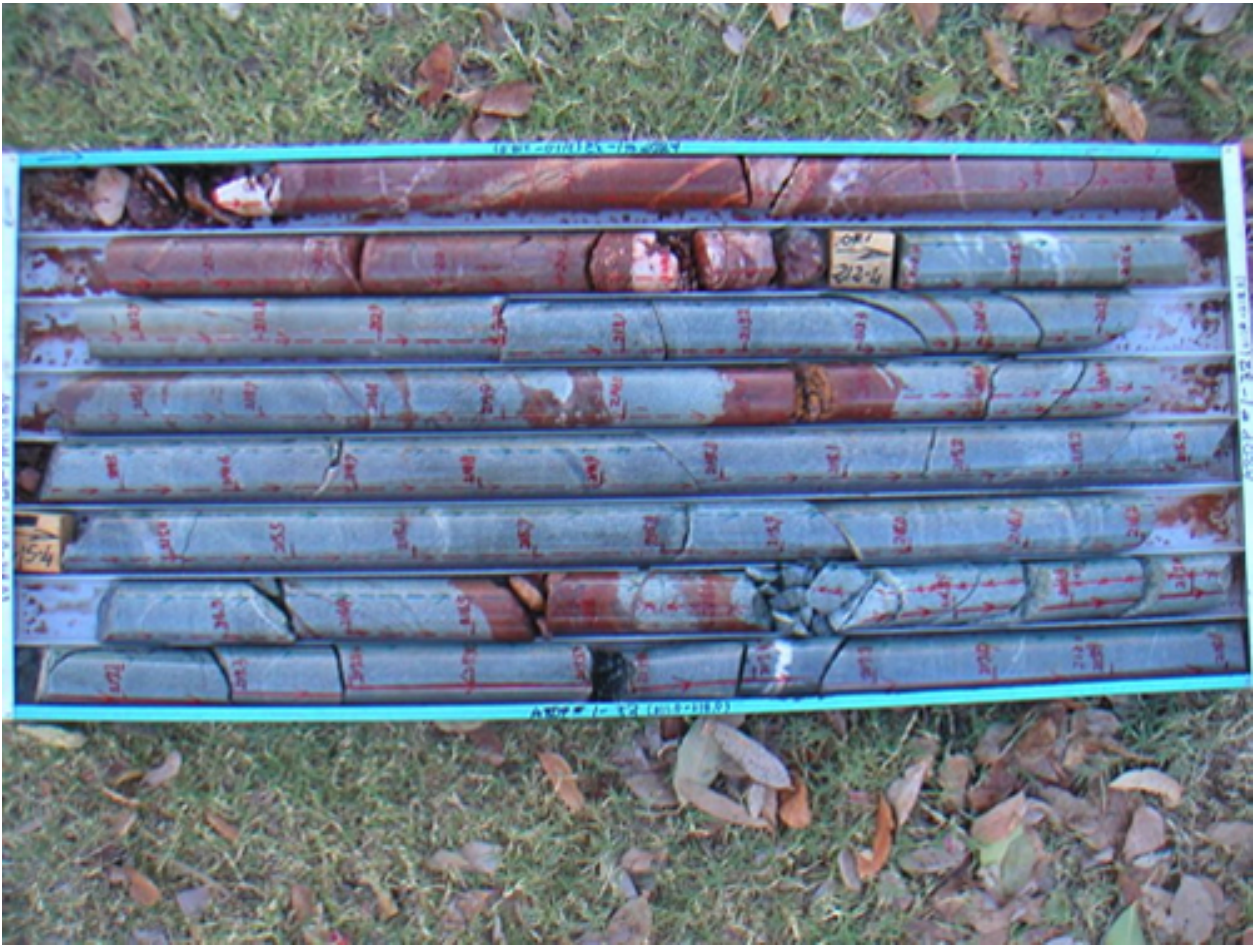


Fig.2 Core samples of hematized basalt obtained from a depth of 211.0~218.0 meters below the present land surface

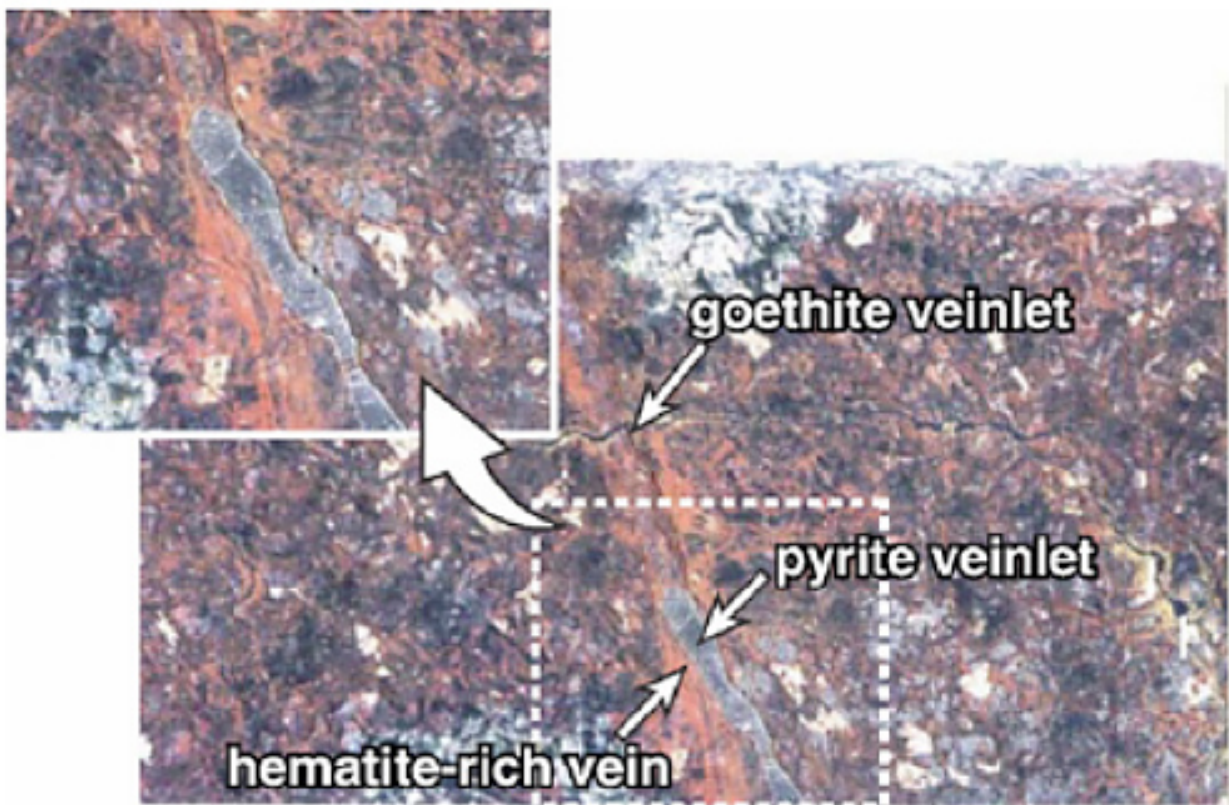
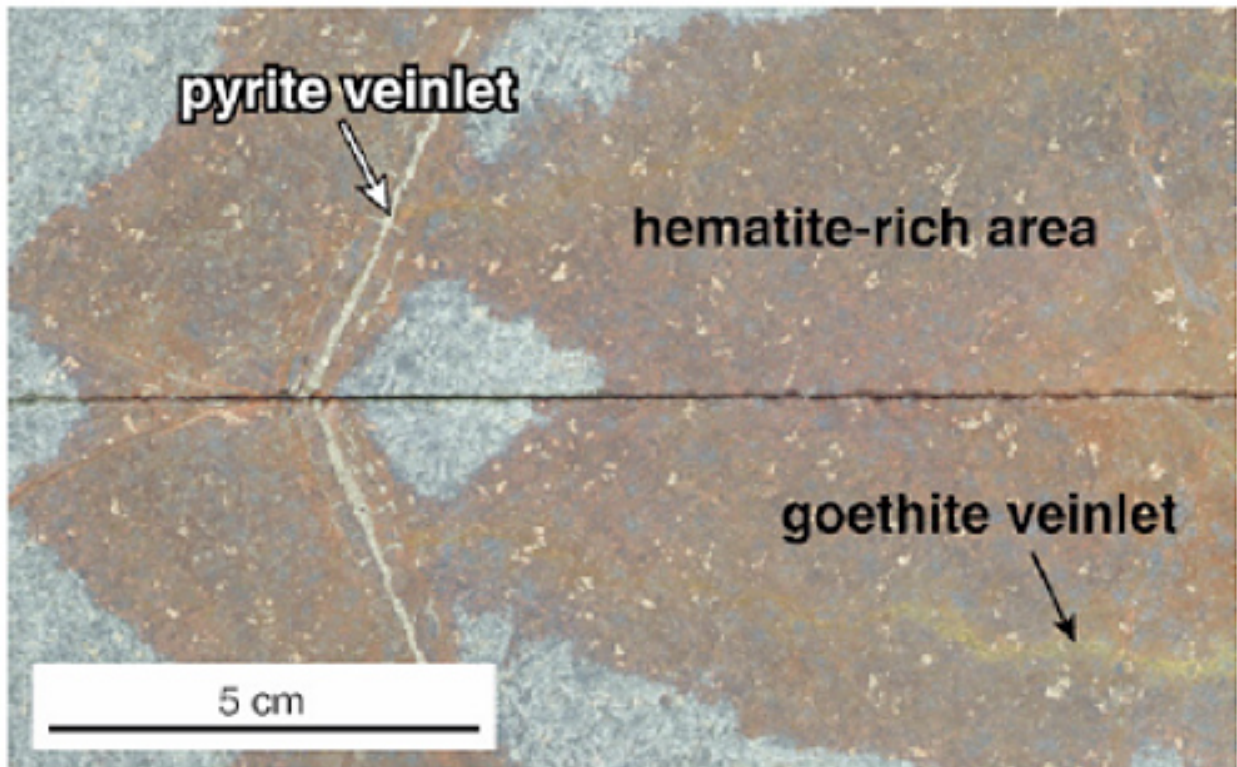


Fig.3 Pyrite veinlets cross-cutting hematized basalt(upper)
A pyrite veinlet diagonally cross-cutting the hematite-rich vein(below)

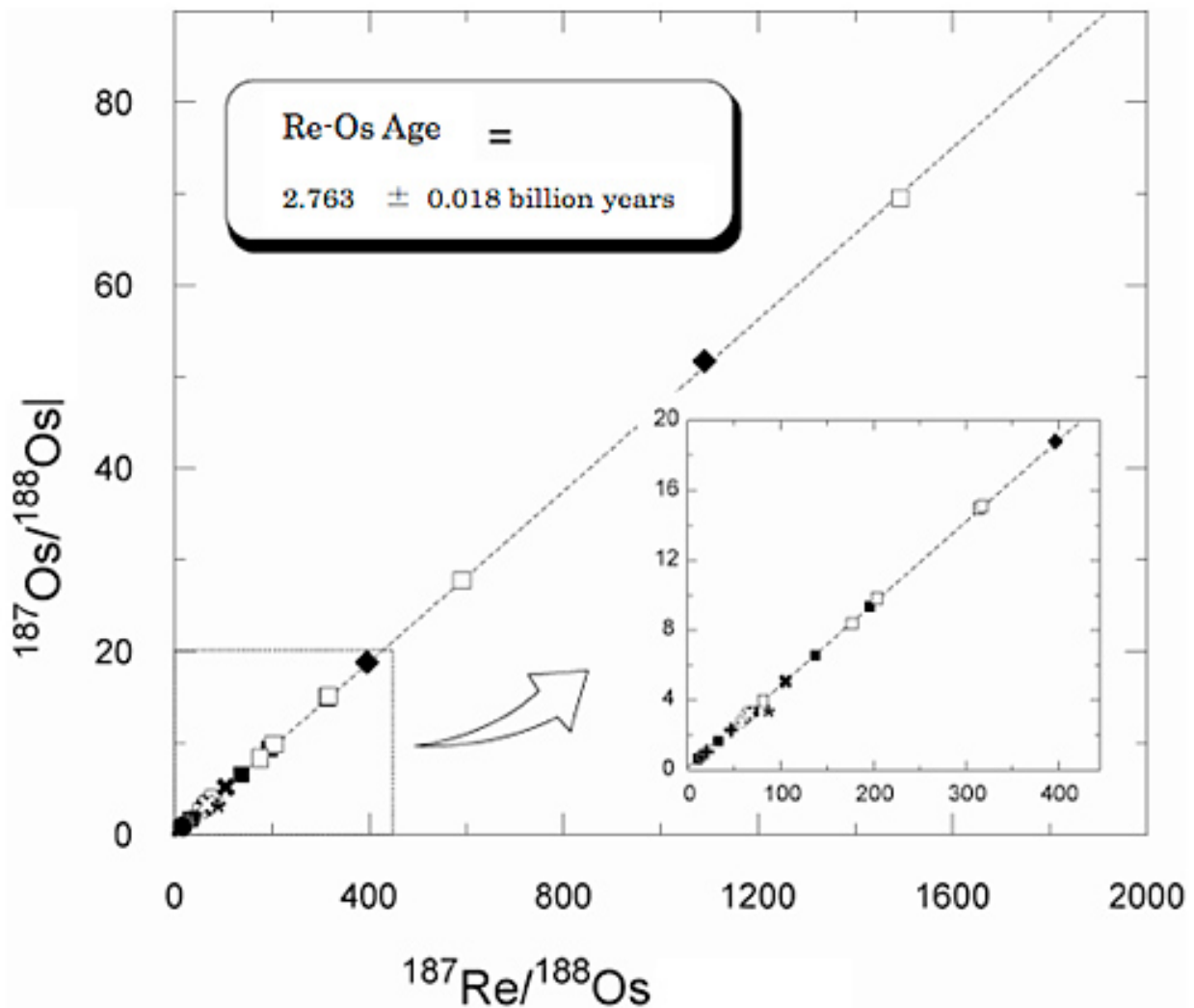


Fig.4 $^{187}\text{Re}/^{188}\text{Os}$ - $^{187}\text{Os}/^{188}\text{Os}$ diagram

It is considered that pyrite had the same initial $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio at the time of formation. On the other hand, the $^{187}\text{Re}/^{188}\text{Os}$ isotope ratios of pyrite vary significantly. All data points would plot on the horizontal line at the time of formation. According to a time interval after the pyrite formation, $^{187}\text{Re}/^{188}\text{Os}$ decreases and $^{187}\text{Os}/^{188}\text{Os}$ increases due to the decay of ^{187}Re to ^{187}Os with the uniform decay constant. In other words, the inclination of the straight line increases in proportion to the time interval. The time interval from the pyrite formation to the present is calculated from this inclination. The age of 2.763 billion years is the result of this calculation on the above diagram.

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