海外特別研究員最終報告書

独立行政法人日本学術振興会 理事長 殿

採用年度 平成30年度 受付番号 201860763 齊藤 京介 氏 名

(氏名は必ず自署すること)

海外特別研究員としての派遣期間を終了しましたので、下記のとおり報告いたします。 なお、下記及び別紙記載の内容については相違ありません。

記

1. 用務地(派遣先国名) 用務地: マサチューセッツ工科大学(国名: 米国)

 研究課題名(和文)<u>※研究課題名は申請時のものと違わないように記載すること。</u> ペルム紀末―中期三畳紀の地球環境変動

3. 派遣期間: 平成30年4月1日 ~ 令和2年3月31日

4. 受入機関名及び部局名

Massachusetts Institute of Technology, Department of Earth, Atmospheric, and Planetary Sciences

 5. 所期の目的の遂行状況及び成果…書式任意 書式任意(A4 判相当3ページ以上、英語で記入も可) (研究・調査実施状況及びその成果の発表・関係学会への参加状況等) (注)「6. 研究発表」以降については様式 10-別紙 1~4 に記入の上、併せて提出すること。

Project title: Biotic and environmental changes spanning the latest Permian-Middle Triassic

I have done three projects during this abroad study. First project is related to evaluation of biomarker syngeneity of Permian-Triassic sections from the Nanpanjiang Basin, South China where most important sections for the end-Permian mass extinction event are exposed. Second project is related to ultra-high resolution study on the end-Permian mass extinction event. Third project is related to preservation of organic matter in sulfidic environments. Here I introduce one by one as following.

[Biomarker syngeneity project at Massachusetts Institute of Technology] The end-Permian mass extinction is the largest mass extinction event. There has been growing interests in Permian-Triassic boundary sections in the Nanpanjiang basin, South China due to the exposure of fossil-rich sections in this region. In this project, I conducted, for the first time, an assessment on biomarker syngeneity with Permian-Triassic boundary samples from the Nanpanjiang Basin. Samples I selected cover both microbialite and micrite dominant facies from shallow water and black shale dominant facies of deep water origin. These geographically and lithologically diverse sections in the Nanpanjiang basin make us possible to conduct basinal scale biomarker syngeneity test.

In this project, I deployed micro-ablation technique to prepare samples in order to efficiently remove potential contamination. By using this technique, I separated rock samples into exterior and interior layers and special efforts were made in comparing biomarker concentration between exterior and interior layers. Various biomarker compound classes such as *n*-alkane, hopane, sterane, and carotenoids are detected in both exterior and interior of the sedimentary rocks from the examined sections. Absent of color for all extracts, I observed higher biomarker concentrations in the exterior than the interior layers. Strikingly, oleanane, which is a biomarker for angiosperm, was also detected in all layers despite of its emergence in Cretaceous. The presence of oleanane and concentration gradients between interior and exterior probably suggest that biomarker contamination has penetrated through the rock surface in the past time, negating the potential application of these samples for syngenetic organic geochemical analysis. Therefore, the Nanpanjiang Basin, South China is a critical region for studying the Permian-Triassic mass extinction event, unfortunately, it is unlikely a suitable candidate for biomarker study.

Through this project, I've learned how to process and to evaluated four fractions of organic matter in order to test syngeneity of organic matters in sedimentary rocks. These knowledge and technique will be especially important to apply older rocks those that tends to be high risk with respect to contamination. When I handle with such samples in the near future, I would like to apply these knowledge and technique.

[Ultra-high resolution study at Bremen University]

The end-Permian mass extinction event has been most intensively studied among mass extinction events and a variety of means has been applied to elucidate causes and processes of the mass extinction event. However, there remains unclear that at ultra-high resolution, how changes in environments correlate with the mass extinction event. Previous studies were at thousand years scale.

In this study I tried to reveal changes in environments near the mass extinction event at decadal-hundred years scale, and then compared the ultra-high resolution data obtained by this project with the conventional low resolution data with thousand year scale, which are obtained by previous study. The result shows that stratigraphic distributions of organic molecules at ultra-high resolution data generally well fit with that of low resolution data. However, the

ultra-high resolution data was able to show presence of multiple events in a thousand year scale peak. One limitation for the ultra-high resolution data is that organic compounds found in the low-resolution data are not always detectable in the ultra-high resolution data. Further methodological development which increase in detectable compounds at ultra-high resolution would be highly appreciated. Nevertheless, the ultra-high resolution data obtained in this project can already enough tell more detailed mass extinction processes and probable causes that were not previously undiscussed.

In addition to organic compounds data at ultra-high resolution, an ultra-high resolution study with respect to trace elements was also made on the same sample set. Because each spot analyzed for trace elements are also at ultra-high resolution, detection limits for each element are more critical. Most of rare earth elements are below detection limits. However, some of major elements are still detectable at this resolution. These elements include iron, aluminum, and sulfur. Evaluations on siliciclastic inputs and redox changes were evaluated by both organic molecules and trace elements at ultra-high resolution, that show generally good agreements between them. This project is still on-going and needs to be proceeded more to submit a paper. I am going to submit the result in this year. Consequently, my purpose of my stay in abroad will be achieved soon.

Through this project, I've learned how to prepare and measure a sample for the ultra-high resolution study. I've also learned how to process the data obtained at such high resolution, using by a multi-paradigm numerical computing environment and proprietary programming language (i.e. MATLAB). In comparison with conventional low resolution data, the data size of the ultra-high resolution data is hundreds to one thousand times higher. Therefore, this data processing skill by the software was mandatory for me, and would be very helpful for handling with such large data set in the near future.

[Desulfurization study at Massachusetts Institute of Technology]

Mass extinction events are often related to environmental disturbances. Among the various environmental deterioration events, oceanic euxinia following deoxygenation of ocean has been especially paid attention to as one of driver of mass extinctions. A lot of efforts on revealing the redox history has been made for mass extinction events, using by elemental abundances, biomarkers, elemental isotopes, and so on. However, there are little known about how the preservation of organic matter is biased in such environment, and it is unknown whether changes in environments at the mass extinction time revealed by organic matter exactly reflect realistic environmental disturbances or not because such the mass extinction event are often accompanied with oceanic euxinia, thereby potentially introducing the bias. Since previous experimental study shows organic matter with specific functional groups react with reduced sulfur species, it is highly possible that organic matter extracted from bulk rock is biased by this sulfurization process. Therefore, it might need to desulfurize organic matter from macro molecules in order to reveal more realistic changes in environments.

Here I applied desulfurization technique first to sulfur rich standard to establish the desulfurization methods and then secondly to the mass extinction event rocks. The standard was prepared from several tens of samples which are enriched in sulfur. And then the standards were divided into several ten vials. A bunch of desulfurization tests were made on the standard until a consistent result through the several tests were achieved. Two criterions to evaluate the consistency were applied here. First one is whether a biomarker distribution after the desulfurization are consistent between the several tests or not. Second one is whether multiple sulfur isotopes based on sulfur species released via the desulfurization experiments on the standard show consistent values or not. Usually desulfurization experiments are evaluated only by the distribution of biomarker. Therefore, these criterions here is stricter with respect to evaluation on consistency of the desulfurization experiment. Completeness of desulfurization

of the standard are also checked by disappearance of sulfur-containing compounds which are originally present in the standard. To conduct efficiently the test, six apparatus has been established in the laboratory, which enable six standards to be processed at the same time.

Through the initial multiple tests, it turned out to be difficult to get consistent result. As expected, to obtain consistent sulfur isotope values from the desulfurization experiment were much more difficult compared to get consistent desulfurized biomarker distribution. Even though the same standard was used for the desulfurization experiment, the sulfur isotope values varied. Obviously, there is sulfur isotopic fractionation when organic molecules are desulfurized from macro molecules enriched in sulfur. Through the multiple improvement on the experiments based on several tens of desulfurization tests, the sulfur isotopes values showed consistent values, thereby successfully establishing nice experimental method for the desulfurization.

The next problem after the desulfurization is to reduce organic matters. Because the reaction of desulfurization is radical process, when a C-S bond breaks, it produces carbon radical, which abstracts a hydrogen atom from the next atoms. This ultimately oxidizes the desulfurized molecules. Some desulfurized organic molecules are heavily oxidized through this process and are not amendable to measure by gas chromatography mass spectrometry. Therefore, reduction is required for these compounds. To reduce these desulfurized molecules is relatively easily done with conventional reduction methods. However, to reduce these desulfurized molecules without destroying them are hard with the methods. This means that quantitative evaluation is hard to made with conventional reduction methods. To discuss changes in paleoenvironments always accompanies with stratigraphic distribution of particular compounds. If the yields are not good for the reduction methods, then it is difficult to assess changes in paleoenvironments because of lacking of good quantified data. Therefore, to establish a method to reduce the desulfurized molecules without destruction is critically important in order to discuss changes in paleoenvironments.

Through the bunch of tests, it turned out that some of desulfurized molecules are destroyed (low yields) by the reduction and they have no longer original carbon skeleton. I tested various things in order to reduce these desulfurized molecules and found that one method can stabilize the molecules and can reduce them without destruction. In another project conducted by other member of the laboratory, the method was applied to organic compounds extracted from algal cultures and successfully found new compounds which were previously not found in that project. Thus, this method achieved a multiple success here.

After these methodology establishment for desulfurization and reduction on the standard sample, seven samples deposited in the end-Permian mass extinction time were at last processed with these methods. At the end-Permian mass extinction events, there are a number of previous studies showing deoxygenation events in the contemporaneous ocean in the studied region must have been accompanied with reduced sulfur species which reacts with organic compounds. As a comparison, Cretaceous samples were also processed.

Contrary to expectations, there are little/no organic compounds released from the examined samples. Because there is a successful desulfurization report on Permian age rocks, this unexpected result would be attributed to a nature of the examined samples. Since carbon-sulfur bonds generally weaker than carbon-carbon bonds, it is most probably that desulfurizable carbon-sulfur bond in the examined samples has already gone from the macromolecule and no desulfurization reaction occurred. This means whether desulfurization experiments work or not depends on a maturity of an examined sample. The samples examined here are already relatively high maturity and desulfurizable compounds by the designed experiments were probably already released into a fraction which is extractable by conventional methods. This result also verifies that previous results based on organic matter might not be biased.