Redox of the latest Proterozoic-Early Paleozoic deep ocean: Moessbauer spectroscopic analysis of deep-sea chert

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The secular change in atmospheric composition, in particular the oxygen concentration, has likely controlled the course of biological evolution. In the Neoproterozoic, the atmospheric oxygen concentration rose immediately before the appearance of large animals, and the anoxic Precambrian deep ocean turned into oxic for the first time, although the details of the oxidation level and process are still not clear.

Mid-oceanic deep-sea sediments that cover extensive areas of the Earth's surface preserve global environmental record on average. As the pre-Jurassic seafloors have already been lost by oceanic subduction, records from deep sea older than 200 Ma are available only in deep-sea chert in ancient accretionary complexes.

We focused on some latest Proterozoic-Early Paleozoic deep-sea cherts from accretionary complexes in Wales, UK (Neoproterozoic), Gorny Altai Mtn., S. Siberia (Ediacaran-Cambrian), Newfoundland, E. Canada (Ordovician), and Bayanhongor, Mongol (Devonian). We applied ^{57}Fe Moessbauer spectroscopy to analyze these cherts for identifying iron species and for checking redox state of deep ocean in the Neoproterozoic-Early Paleozoic.

The curve fitting of Moessbauer spectra was performed, assuming that the spectra were linear combination of peaks, and Moessbauer parameters (i.e., isomer shifts, quadrupole splittings, and internal magnetic fields) were obtained. By comparing these parameters to the standards, we identified 3 chemical states of iron in all the samples; one sextet and two doublets, showing hematite (Fe_2O_3), paramagnetic Fe^{3+}, and paramagnetic Fe^{2+}. One un-identified iron species is detected a little in the sample from Gorny Altai Mtn.. Peak positions of pyrite (FeS_2) were constrained, since the peak positions of paramagnetic Fe^{3+} and pyrite are in very close proximity.

The analytical results show that the main iron-containing mineral in all samples is hematite that is characterized by a significant sextet pattern in Moessbauer spectra. This suggests that the latest Proterozoic-Early Paleozoic deep ocean was essentially 'oxic'. The term 'oxic' is used here as 'relatively oxidizing condition than the redox potential of Fe(III)/Fe(II) transition'. In the latest Proterozoic-Early Paleozoic deep-sea, ferric iron was likely stabilized first as iron-hydroxide, and changed into hematite through diagenesis. It is noteworthy that pyrite with ferrous iron was not detected at all in all samples.

The present result suggests that oxic conditions in the deep sea have appeared by the latest Proterozoic and persisted throughout the Phanerozoic, except for some unique events such as the Permo-Triassic Superanoxia and Toarcian anoxia. The Precambrian world is generally regarded to have been reducing, but the present result confirmed that the deposition of ferric iron in deep ocean was already available in the latest Proterozoic. By using the same approach to much older deep-sea cherts, we may identify the exact timing of the first deep-ocean oxygenation in the Earth's history.