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Deep-sea anoxia during the Marinoan Snowball Earth

SATO, Tomohiko[1*] ; OKADA, Yoshihiro[1] ; ASANUMA, Hisashi[1] ; MARUYAMA, Shigenori[2] ; SHOZUGAWA, Katsumi[3] ; MATSUO, Motoyuki[3]

[1]Department of Earth and Planetary Science, Tokyo Institute of Technology, [2]Earth-Life Science Institute, Tokyo Institute of Technology, [3]Graduate School of Arts and Sciences, The University of Tokyo

The oxidation of the deep ocean in the Earth's history is regarded to have occurred in the Neoproterozoic, coincident with the metazoan diversification; however, the geological record of the Neoproterozoic environment has been restricted only to shallow-sea sediments. Here we present the discovery of the Neoproterozoic deep-sea sediments in the accretionary complex in Llyen Peninsula, Wales, UK. In the studied section, the oceanic plate stratigraphy consists of mid-ocean ridge basalts, bedded dolostones, ca. 10 m-thick black mudstones, hemipelagic siliceous mudstones and turbidite sandstone, in ascending order. The detrital zircons separated from sandstone give the youngest age of 637+-13 Ma. Within ca. 10 m-thick black mudstones, lithological changes are observed; (1) alternating black mudstone and dolomitic carbonate layers, (2) black mudstone with less developed lamination, (3) pyrite-enriched black mudstone, and (4) rhythmically bedded black mudstone, and gradually turns into bedded greenish gray chert sequence. The overlying greenish gray cherts show red color in some place. We analyzed these mudstones and cherts by 57Fe Mossbauer spectroscopy, and identified six iron species, i.e., hematite, pyrite, two paramagnetic Fe3+, and two paramagnetic Fe2+ with different quadrupole splittings. About a quarter of iron content in the black mudstones consist of pyrite, and other component belong to paramagnetic Fe2+ or occasionally paramagnetic Fe3+. The overlying red cherts contain hematite as the main iron mineral. In the analyzed samples, hematite and pyrite never co-existed. The occurrence of hematite in deep-sea chert essentially indicates a primary oxidizing depositional condition, and that of pyrite a reducing one, respectively. The present results confirmed that a reducing condition persisted in the Neoproterozoic deep-sea through the interval of the black mudstone deposition. The overlying partly-red hematite-bearing cherts give evidence of recover from reducing to oxidizing condition before the arrival to the trench. Here we propose that the black mudstone in Llyen Peninsula shows the global-scale oceanic anoxic event during the Marinoan Snowball Earth, and name this event the 'Marinoan Superanoxia'. During the black mudstone deposition, the whole ocean may have turned into anoxic like the Permo-Triassic boundary Superanoxia; although further discussions for the depositional model based on other geochemical proxies are needed.