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## Mineralogical and geochemical characteristics of pyrite spherulites found in the Nishi Kannondou Kuroko deposit

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Pyrite spherulites are often observed in modern seafloor hydrothermal vents as well as ancient hydrothermal systems. Sulfide spherulite has been proposed as an important material in the origin of life by catalyzing metabolisms or acting like a cell. However, formation processes of the pyrite and their association to biotic processes are not well understood due to a lack of detailed investigations on mineralogical and geochemical characteristics of the pyrite. We have recently found a possible fossil chimney and abundant pyrite spherulites in a small sulfides deposit (Nishi Kannondo deposit), an ancient (ca. 13Ma) seafloor hydrothermal system, in Hokuroku district, Akita Prefecture, Japan. Objectives of this study are (1) to compare the mineralogical and geochemical characteristics of spherulitic pyrite and non-spherulitic pyrite found in the Nishi Kannondo deposit, and (2) to investigate the relationship of the formation of spherulitic pyrite and biological activities.

We collected various ore samples. Pyrite-rich ores are commonly found in western and northern side of the ore deposit. Black ores containing sphalerite and galena are found in the center of the ore deposit, and barite ores are from southern side of the deposit. These lithological variations correspond to the paleo-structures of chimney and mounds. Pyrite spherulites are found in barite-rich ores which may be located at the chimney out wall or mound inside: those were formed in low temperature and sulfate-rich environments, thus in distant from black smoker activities.

Based on microscopic observations, an individual pyrite spherulite, a few mm in diameter, is divided into (a) central, (b) middle, and (c) outer parts. Central and middle parts are mostly composed of radial pyrite crystals. Other sulfide minerals (e.g., chalcopyrite, tennantite and molybdenite) were also observed in the central part. Middle parts are composed of concentric layers of radial pyrite crystals and other minor minerals (e.g., chalcopyrite, tennantite and molybdenite). In chemical mapping of the pyrite layers, concentric zonings of As and Cu were observed from central to middle parts. Outer parts are composed of cubical pyrite aggregates. These characteristics of pyrite spherulites indicate that the pyrites record periodical rapid and slow precipitation processes. We also propose that these characteristics of pyrite spherulite reflect changes in surrounding environments during the formation of pyrite spherulites, such as repeated dissolution and precipitation of sulfates in chimney or mounds.

Samples containing abundant pyrite spherulites are also enriched in organic carbon content (up to 1.6 wt%), compared to those mostly containing non-spherulitic pyrite. S isotope analyses of these samples showed that S isotope compositions of pyrite spherulites were about 15 per mil lighter than those of non-spherulitic pyrites. This indicates that hydrogen sulfide for the formation of pyrite spherulites was supplied through bacterial sulfate reduction. Therefore, our preliminary investigation suggested that biological activities were related to the formation of pyrite spherulites.

Keywords: pyrite, spherulite, kuroko, organic carbon, bacterial sulfate reduction