## Thermal alteration of kerogen by post-Kuroko submarine hydrothermal fluids: its implication of diagenesis of M2 mudstone

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The Kuroko deposits in the Hokuroku District are overlaid by mudstone (M2). This M2 mudstone was altered by the post-Kuroko submarine hydrothermal activities causing interaction between submarine hydrothermal fluids and organic matter. Such interaction probably caused a relatively unknown geochemical processes such as thermochemical sulfate reduction and generation of hydrothermal petroleum.

Carbonaceous M2 mudstones were collected from the Matsumine mine (Dowa collection), Ishinosawa (I section) and Daimyojin (D section). I and D sections are continuous section from Fukazawa mine. Concentrations of organic carbon and pyrite sulfur were determined on collected samples. Kerogen was also extracted from seven samples and their compositions and carbon isotope ratios were determined.

The M2 mudstone from the Matsumine mine was essentially clastic sediments forming the concretion texture. The concentrations of total organic carbon (TOC) were up to 0.51wt%. H/C ratios of kerogen were extensively and thermally altered by post-Kuroko submarine hydrothermal activities. Calcite, pyrite and anhydrite coexist in the concretion sample at the Matsumine mine. A model of thermochemical sulfate reduction (TSR) explains the genesis of above coexisting minerals, reducing dissolved sulfate from seawater by organic matter into bicarbonate.

Samples from the I section also show the hydrothermal alteration feature, such as a pyrite-quartz vein and silicification. H/C ratios of kerogen were low suggesting the thermal alteration caused by the post-Kuroko submarine hydrothermal activities. On the contrary, H/C ratios of kerogen were not low in the D section where the framboidal pyrite were present and any hydrothermal veins were absent. This suggests that thermal alteration of kerogen was limited only around the Kuroko ore deposits.

The stable carbon isotope compositions of kerogen were rather homogeneous (-22.9 to -22.2) among examined samples. H/C vs delta <sup>13</sup>C diagram suggests that kerogen released low H/C ratio hydrocarbons, such as petroleum, rather than methane during the thermal alteration. Fractions of such hydrocarbons (F in the Rayleigh distillation equation) compared to remaining kerogen are necessary to be high, implying large amounts of hydrothermal petroleum released from M2 mudstone during diagenesis, probably affecting syngenetic microbial activities in the ancient Japan Sea.