Significance of thermochemical sulfate reduction for the genesis of volcanogenic massive sulfide deposits: Case studies on 2.7 Ga Potter mine and 15 Ma Kuroko deposits

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Thermochemical sulfate reduction (TSR) is one of the major pathways for generating hydrogen sulfide in submarine hydrothermal systems. Recent studies propose that TSR occurs in sediments heated by hydrothermal fluids and plays a significant role in forming volcanogenic massive sulfide (VMS) deposits. However, geological, and geochemical evidence to support this model is still scarce.

Here, we report the outcome of our investigation of two 15Ma Kuroko VMS deposits in Japan, with a 2700Ma Potter mine in Canada. They show similar sulfide mineral assemblages and some ores are disseminated into carbonaceous sedimentary rocks associated with calcite and barite.

The $\delta^{13}C_{V-PDB}$ values of sedimentary carbonates from the 15Ma Kuroko deposit varied from -6 to -3‰, suggesting organic and inorganic carbon mixing occurred. The $\delta^{34}S_{V-CDT}$ values of Kuroko barites were from +21 to +25‰. Such a shift to heavier $\delta^{34}S$ values is likely caused by sulfate reduction in sediments followed by Rayleigh fractionation. These lines of evidence support that TSR occurred in shallow sediments in the hydrothermal area.

The ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values of Kuroko barites, from 0.7060 to 0.7075, indicate a mediate value of Miocene seawater and hydrothermal fluids. The unconventional $\delta^{88/86}$ Sr values were also measured, ranging from -0.1 to +0.07‰ (relative to SRM987, NIST). Such values most likely suggest a significant contribution from ${}^{88}\text{Sr}$ -rich endmember, i.e. sediments. Therefore, the two types of Sr isotope data also support the TSR model for forming VMS deposits.

From the 2700Ma Potter mine, very negative $\delta^{13}C_{V-PDB}$ values of hydrothermal carbonates were found, ranging from -20 to -4‰, indicating the occurrence of oxidation of organic matter or CH₄. Sulfate ions were plausible oxidants in the hydrothermal area. The $\delta^{88/86}$ Sr values of these carbonates are more variable, ranging from -0.4 to +0.3‰, compared to those of Kuroko values. This implies more contribution from sedimentary ⁸⁸Sr. These results suggest that TSR has triggered the formation of VMS deposits even in Archean hydrothermal systems. Additional verification of mass-independent fractionation of sulfur (MIF-S) in Potter sulfides showed a positive correlation with samples having TSR signatures. This implies that the TRS could cause MIF-S in the sediment-hydrothermal interaction zone.