

Sulfur isotopic evidence for the origin of elemental sulfur in gas hydrate-bearing sediments of the northern South China Sea

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Elemental sulfur is a common intermediate in the sulfur cycle and contributes significantly to the fractionation of stable sulfur isotopes in different reservoirs in shelfal marine sediments (e.g., Canfield and Thamdrup, 1994). However, no study dedicated to the isotopic composition of elemental sulfur in seep environments has been conducted to the best of our knowledge, thus limiting further insight into the biochemical pathways involving elemental sulfur in such environments. In this study, elemental sulfur and pyrite were extracted from the sediment of a 200-m long gas hydrate-bearing core, which was obtained from the gas hydrate drilling expedition to the northern South China Sea in 2013 (Zhang et al., 2015). The sulfur isotopic composition of elemental sulfur was found to vary from -16 to +23 per mill, and pyrite yielded values ranging from -34 to +18 per mill. Interestingly, elemental sulfur revealed higher ³⁴S contents (up to 30 per mill) than the associated pyrite in most sediment layers. Since elemental sulfur is only produced during oxidative pathways in the sulfur cycle, the studied elemental sulfur apparently represents the oxidation product of hydrogen sulfide by various electron acceptors such as Mn(IV) oxides or Fe(III) oxides (e.g., Thamdrup et al., 1993; Yao and Millero, 1996). Since there is little sulfur isotope fractionation for oxidative processes (Fry et al., 1986), the enrichment of elemental sulfur in ³⁴S points to a pool of hydrogen sulfide depleted in ³²S, which is best interpreted to result from sulfate-driven anaerobic oxidation of methane.

References:

Canfield D.E. and Thamdrup B. (1994) The production of ³⁴S-depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* **266**, 1973.

Fry B., Cox J., Gest H. and Hayer J.M. (1986) Discrimination between ³⁴S and³²S during bacterial metabolism of inorganic sulfur compounds. *J. Bacteriol.* **165**, 328–330.

Thamdrup B., Finster K., Hansen W. and Bak F. (1993) Bacterial disproportionation of elemental sulfur coupled to chemical reduction of iron and manganese. *Appl. Env. Microbiol.* **59**, 101–108.

Yao W. and Millero F.J. (1996) Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. *Mar. Chem.* **52**, 1–16.

Zhang G., Liang J., Lu J.A., Yang S., Zhang M., Holland M., Schultheiss P., Su X., Sha Z., Xu H., Gong Y., Fu S., Wang L. and Kuang Z. (2015) Geological features, controlling factors and potential prospects of the gas hydrate occurrence in the east part of the Pearl River Mouth Basin, South China Sea. *Mar. Pet. Geol.* **67**, 356–367.