

## Isotopic composition of sulfur in gypsum deposits that relate to sulfidic springwaters

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Hydrogen sulfide is one of the most common gases in springwaters related to limestone caves. Such hydrogen sulfide is produced by bacterial sulfate reduction and has a lower  $d^{34}\text{S}$  value than sulfate. The oxidation of  $\text{H}_2\text{S}$  to  $\text{H}_2\text{SO}_4$  promotes the corrosion of wall rocks and induces the deposition of gypsum. Gypsum deposits are often observed as a crust covered on limestone cave-walls above the watertable of  $\text{H}_2\text{S}$ -springwaters (e.g., [1]). These vadose gypsum crusts have a  $d^{34}\text{S}$  value similar to that of  $\text{H}_2\text{S}$  in the springwater (e.g., [1]). This observation implies that sulfate in these gypsum crusts is supplied by the  $\text{H}_2\text{S}$ -oxidation that occurs above the watertables. The oxidation of  $\text{H}_2\text{S}$  must occur also below the watertables; however sulfate produced below the watertable cannot preserve its isotope signature with  $^{34}\text{S}$ -depletion, because sulfate produced from  $\text{H}_2\text{S}$  should be mixed with sulfate in the springwater. As  $^{34}\text{S}$ -depleted gypsum crusts can be obtained also in the caves where the emission of  $\text{H}_2\text{S}$  from the springwater ceases (e.g., [1]), the  $d^{34}\text{S}$  values of these gypsum crusts can be used to estimate the  $d^{34}\text{S}$  values of  $\text{H}_2\text{S}$  for the ancient springwaters. As the  $d^{34}\text{S}$  values of  $\text{H}_2\text{S}$  in the springwaters are controlled by the activity of sulfate-reducing bacteria, the  $d^{34}\text{S}$  values of these vadose gypsum deposits can be used as a paleoindicator for environmental factors that affect the bacterial activity. Recently Maruoka et al. [2] reported that isotope differences between sulfate and sulfide are controlled primarily by the temperature of springwaters. Therefore, we may obtain the thermal history of sulfidic springwaters using the  $d^{34}\text{S}$  values of vadose gypsum deposits of different ages. Actually, a wide range of  $d^{34}\text{S}$  values is observed for gypsum deposits in the Frasassi caves in Italy. Based on the isotopic composition, we can discuss the thermal history of the springwaters related to these caves.

[1] Galdenzi, S., Maruoka, M. (2003), *J. Cave Karst Stud.* 65 111-125.

[2] Maruoka, M., Galdenzi, S., and Matsuda, J. (2007) *Goldschmidt Conference Abstracts 2007*, A631