S-isotope determination of nano-pyrites by NanoSIMS imaging: application to biominerals in precambrian stromatolites.

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Sulfur isotopes constitute a powerful tool to identify microbial metabolisms in the sedimentary record and in old rocks. Many bacterial species have been shown to induce the formation of pyrite or its precursors. However, their small size, generally less than 1 micron, is a serious obstacle to the determination of their isotope signature.

The NanoSIMS has been shown to be fully capable of measuring $\delta^{34}S$ in pyrite on 1.5 micron large areas [1] and even $\delta^{33}S$ if the analyzed area is increased to 15 microns [2]; but significant data corrections are required. To be able to investigate the nano-pyrites (size from 200 nm to 1 micron) in the Tumbiana stromatolite, we developped a protocole for precise determination of $\delta^{34}S$ by NanoSIMS imaging [3] using electron multipliers, which allows us to obtain isotopic measurements of pyrite grains only a few 100 nm wide. Our method requires thorough evaluation of the QSA effect on the instrument [4] in addition to the precise determination of instrumental biases, using well characterized standards. We have compared the behavior of two different instruments, the NanoSIMS 50 at the Muséum of Natural History in Paris and the NanoSIMS 50L in Lausanne. Correction factors, including the QSA factor, varied from one session to another on both instruments, high-lighting the need to determined instrumental effects in each session.

Subsequent NanoSIMS analyses of $\delta^{34}S$ in the Tumbiana nano-pyrites revealed a large range of values from -34 ‰ to 51‰. Such large range is interpreted to be the consequence of Rayleigh distillation of sulfate available for microbial sulfato reduction in the sediment during the early diagenetic process [3].

[1] Nishizawa et al. 2010 RCM, 24, 1397-1404. [2] Hauri et al. 2016 Chemical Geology, 420, 148-161. [3] Marin-Carbonne et al. 2018 Geobiology, 16, 121-138. [4] Slodzian et al. 2004 Applied Surface Sci. 231, 874-877.