

Detecting intermittent events of microbial activity in the subsurface using microscale stable isotope analysis and radiometric dating

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The stable isotope signature of authigenic minerals has been frequently used to decipher active and ancient microbiological activity in various subterranean environments including deep sea sediments, subseafloor basalts, and from the crystalline continental crust. Ancient microbial processes described from the fractured upper continental crust include methane generation and oxidation and the findings are based on the isotope composition of authigenic calcite and pyrite that formed when methane was generated (¹³C-rich calcite) or when it was consumed by anaerobic oxidation (AOM, featuring ¹³C-poor calcite) coupled to bacterial sulfate reduction (BSR, featuring pyrite with diagnostic $\delta^{34}\text{S}$ values)¹. Timing of these processes have so far been elusive due to the fine-grained and zoned nature of these minerals have inhibited direct dating.

Here we apply recently developed microscale techniques for intra-crystal SIMS analysis/imaging of stable isotopes and for radiometric dating (*in situ* Rb-Sr² and U-Pb³ geochronology analysis of carbonate and co-genetic minerals), coupled with spatially related fluid inclusions and biomarker investigations, for direct timing constraints of the microbial processes. Our *in situ* LA-ICP-MS-based dating represent the first timing constraints of AOM within the crystalline crust, comprising several Mesozoic and Paleozoic events, at various physicochemical conditions. Our previous isotope study from the crystalline crust revealed the most ¹³C-depleted calcite ever reported¹. Here we extend the unique isotope inventory of this oligotrophic environment by adding previously unseen isotopic spans and ¹³C- and ³⁴S-enrichment in calcite and pyrite, respectively, along with SIMS-imaging that gives new insight into isotope distillations during microbial processes.

**This abstract is too long to be accepted for publication.
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page.**

[1] Drake et al. (2015), *Nature Comm.* **6**, 7020 [2] Zack & Hogmalm (2016), *Chem. Geol.* **437**, 120-133. [2] Roberts & Walker, 2016. *Geology*. **44**, 531-534