Tracing episodic microbial oxidation of biogenic methane deep in fractured granite using $\delta^{13}C_{calcite}$

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Fossil and active microbial oxidation of methane (AOM) has been described from many settings worldwide, e.g. at cold seeps, and can be traced by extremely depleted $\delta^{13}C$, e.g. of authigenic carbonates (generally -65 to -45‰ [1]). We here show signs of AOM in a substantially less studied environment - deep in fractured granitoids within a shield area (Laxemar, Sweden). Here, the methane gas concentration is currently low, but nevertheless, microbial AOM is evidenced by the most $\delta^{13}C$-depleted calcites ever reported (to our knowledge); down to -125‰ V-PDB (SIMS data). These $\delta^{13}C$ values rule out any other source than biogenic methane. The preferential depth of AOM (-350 to -650 m, cf. [2]) marks the shift from the microbial DOC consumption in the groundwater at shallower depths to methanotrophic at greater depth where DOC is depleted. Marine $\delta^{18}O_{calcite}$ values show that AOM was initiated by intrusion of SO_4^{2-}-rich marine waters causing sulphate reducing bacteria (SRB) to outcompete prevailing methanogens for H_2, and instead methane oxidisers formed concortia with SRB, as shown by SRB-specific biomarkers trapped within the calcites (GC-MS and ToF-SIMS evidence). Low contents of dissolved carbon prevented dilution of $\delta^{13}C_{calcite}$ by other C sources than AOM, explaining why $\delta^{13}C_{calcite}$ is much lower than in other AOM-settings where $\delta^{13}C_{calcite}$>>$\delta^{13}C_{methane}$ [1]. The extremely large intra-crystal $\delta^{13}C$-variation (up to 109‰) and related $\delta^{18}O$-variation show that AOM was episodic and e.g. succeeded by intrusion of sulphate-poor glacial water ending the AOM activity. The discovered deep AOM-zone must therefore be fossil, i.e. $\delta^{18}O$ and $\delta^{13}C$ of the calcites and modern groundwater are uncorrelated, and instead related to a pre-Holocene transgression of marine waters.

[1] Aloisi *et al*.. (2002), *EPSL* **203,** 195-203
[2] Drake *et al*.. (2012), *Geochim Cosmochim Acta* **84**, 217-238

O and Hf isotopic evidence in zircons for crustal recycling in caldera complexes and rifts, Picabo volcanic field, Yellowstone hotspot track

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We report oxygen isotope diversity in zircons of large volume rhyolites of the Picabo volcanic field (10.4-6.6Ma) of the Snake River Plain (SRP), highlighting the generation, by shallow remelting, and rapid assembly of diverse magma batches prior to caldera forming eruptions. *In situ* measurements of ε_{Hf} and $\delta^{18}O$ coupled with U-Pb geochronology and whole rock Sr and Nd isotopes elucidate the processes by which large volumes of rhyolite are produced, starting with large-scale (up to ~40-60%) melting of Archean crust followed by plume driven remelting of volcanics in rift zones and caldera complexes. Similar to Heise and Yellowstone, the Picabo volcanic field produced a series of voluminous rhyolites that become progressively lower in magmatic $\delta^{18}O$ (from 7.9 to 3.3‰) and demonstrate increasing zircon $\delta^{18}O$ diversity through time (from <1‰ in early eruptions to >5‰ in late-stage). In contrast, zircon ε_{Hf} remains relatively homogeneous within units, with average ε_{Hf} ranging from -28 to -5.3 (with rare $\varepsilon_{Hf}(0)$=-47 zircons reflecting pure Archean crustal melts). The temporal trend in $\delta^{18}O$ emphasizes the importance of remelting hydrothermally altered intracaldera rhyolites during caldera burial. However, the early appearance and overabundance of low $\delta^{18}O$ rhyolites suggests that hydrothermal preconditioning of the crust was facilitated by Basin and Range extension and metamorphic core complex formation. The preservation of diverse isotopic signatures in zircon, corroborates the importance of rapid batch assembly and eruption of heterogeneous melts with diverse crystal cargoes. Our interpretations highlight the mechanism by which large volume rhyolites are generated, processes applicable to producing rhyolites worldwide that are facilitated by plume driven volcanism in an extensional tectonic regime. Our newly discovered low-$\delta^{18}O$ rhyolites contribute to the growing database of greater than 10,000 km^3 of low and diverse $\delta^{18}O$ rhyolites of the SRP, advancing our understanding of the 16 million year history of silicic volcanism.

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