Timing and geochemistry of calcite veins in pillow lavas of the Troodos ophiolite: implications for fluid composition and vein mineral growth in a supra-subduction zone

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The Late Cretaceous Troodos supra-subduction zone ophiolite exposes well-preserved and heavily veined pillow lavas that lack an emplacement-related metamorphic overprint and thus represent an outstanding example of fossil fluid circulation through oceanic crust. Minerals precipitated from these paleo-fluids in fractures (veins) and may have inherited geochemical signatures of their source and the prevailing environment.

Based on cathodoluminescence petrography, fluid inclusion microthermometry, rare earth element (REE) and isotope geochemistry (87 Sr/ 86 Sr, δ^{13} C, δ^{18} O, and Δ_{47}), we discuss the potential fluid sources, determine the time and temperature of vein mineral precipitates, and further provide insights into vein mineral growth dynamics using the example of zoned calcites.

Veins were subdivided into (1) syntaxial calcite, zeolite, or quartz veins related to extensional fracturing and being either accompanied by a median line (crack and sealing) or late-stage calcite crystals (incomplete sealing), (2) blocky calcite veins associated with hydrofracturing and host rock brecciation, and (3) antitaxial fibrous calcite veins that formed by diffusion-crystallization processes. Most veins show seawater-dominated REE distribution patterns (e.g., negative Ce and positive Y anomalies) and their 87 Sr/ 86 Sr, δ^{13} C, δ^{18} O, and Δ_{47} isotopic compositions are in agreement with precipitation from seawater at low temperatures ($\leq 40 \, ^{\circ}$ C). A few veins, however, reveal very low 87 Sr/ 86 Sr (~0.7061) and negative δ^{13} C (-5.4 to -10.2 ‰ VPDB) suggesting some contribution of mantle CO₂ from degassing magmas and/or leaching of the host rock. These samples correspond to higher formation temperatures ($\geq 140 \, ^{\circ}$ C) that are inferred from fluid inclusion and clumped isotope measurements.

Calcite formation and fracturing of syntaxial crack and sealing veins are dated by matching their ⁸⁷Sr/⁸⁶Sr ratios with the well-established seawater Sr isotope curve. Low temperature vein mineralization was predominantly driven by hydrofracturing and host rock brecciation and took place between 91.5 and 82.5 Ma. The succeeding phase of low temperature antitaxial fibrous calcite vein growth from 75.0 to at least 64.9 Ma temporally overlaps with the rotation of the Troodos microplate which might be reflected by prominently curved calcite fibers. The young age (22.7 Ma) of a late-stage calcite sample coinciding with initial uplift is as unique as its flat REE distribution pattern without any Ce anomaly. High temperature calcites are assumed to have been precipitated shortly after host rock solidification in order to provide sufficient heat to increase the temperature of circulating fluids up to 210 °C. They are characterized by Mn-controlled oscillatory growth zonation that is partly interpreted as closed-system geochemical self-organization. Mn-rich growth zones correlate with higher $\delta^{18}O$ (-4.1 to -9.9 % VPDB) and accumulations of decrepitated fluid inclusions due to isobaric cooling, while significantly lower $\delta^{18}O$ (-17.3 to -22.3 % VPDB) is restricted to Mn-poor zones with well-preserved fluid inclusions. This elemental and stable isotopic zonation including variations within individual growth zones may be related to disequilibrium precipitation.

This study is financially supported by the Austrian Science Fund (FWF-P 27982-N29).