The clumped-isotope geochemistry of marble exhumation

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Exhumation and accompanying retrograde metamorphism alters the compositions and textures of metamorphic rocks through deformation, water-rock reactions and closed-system diffusion-controlled processes. Here, we combine measurements of $\delta^{13}C$ and $\delta^{18}O$ values with carbonate clumped-isotope thermometry to relate deformation and mineralization events of marbles to their retrograde thermal history; and to distinguish between open- and closed-system processes. We sampled calcite and dolomite marbles from the core-complex of Naxos (Greece), where peak temperatures ranged from ~400 to 700 °C.

Color-banded calcite marbles record the conditions of retrograde deformation events: In one sample, white and grey calcite layers have Δ_{47} values of 0.362-0.372‰ and 0.402-0.409‰ (in the absolute reference frame), respectively, and a uniform $\delta^{18}O$ and $\delta^{13}C$ values. We propose that the Δ_{47} values of white layers reflect the diffusion-controlled apparent blocking temperature of clumped-isotope re-ordering during slow cooling (~250˚C), whereas those of grey layers reflect dynamic recrystallization at lower temperatures (~190˚C). Here, deformation occurred in a closed system. In a different sample, Δ_{47} values are negatively correlated with $\delta^{18}O$ and $\delta^{13}C$ values, suggesting fluid-rock reaction was associated with dynamic recrystallization at ~70 ˚C.

In contrast to calcite marbles, dolomite marbles generally have lower Δ_{47} values that reflect its higher clumped-isotope blocking temperature (~300 ˚C). However, some Naxos dolomite marbles contain secondary dolomite veins that record higher temperatures up to 370 ˚C. This finding requires a brief, hot hydrothermal event, were high-temperature fluids infiltrated an initially cooler rock, which presumably experienced a brief, spatially restricted, thermal shock and cooled down before slow diffusionally-controlled processes could alter Δ_{47} values far from the veins. This scenario is supported by the finding that veins are 4 ‰ lower in $\delta^{18}O$ and 1.5 ‰ lower in $\delta^{13}C$ than the host rock, which indicates mineralization from an isotopically light fluid, and host dolomite immediately in contact with the veins have lower Δ_{47} values, but no change in $\delta^{18}O$ or $\delta^{13}C$ values.