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Cryptic secondary cementation of Ordovician limestones in the Baltoscandian Basin, northern Europe, revealed through trace-element mapping and U-Pb dating by LA-ICP-MS

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Primary phases in carbonate rocks archive a wealth of geochemical information about depositional conditions and environmental changes. Secondary phases may record additional—albeit more cryptic—information, potentially complicating interpretation of primary signatures. The ability to compositionally characterize and date multiple, texturally distinct generations of primary, diagenetic, and metamorphic carbonate phases enables deciphering of complex depositional and post-depositional histories carbonate successions have experienced. Combined trace-element mapping and U-Pb geochronology of calcite *in situ* (in thin sections) by LA-ICP-MS provides opportunities to assign absolute ages to calcite crystallization and recrystallization with petrographic and geochemical context. We have applied this approach to two samples of apparently pristine, unmetamorphosed Ordovician bioclastic limestones from the Viki drill core (western Estonia), representing the eastern part of the Baltoscandian Basin. The depositional ages of the samples are constrained by biostratigraphic correlation to ca. 460 and 445 Ma (Hints et al., 2014). Several lines of evidence—such as very low organic-matter maturation and properties of clay minerals—indicate that this sequence did not experience temperatures above 100 °C, and likely not above 50 °C, since deposition (Kirsimäe et al., 2020). Optical petrography and backscatter-electron (“BSE”) imaging reveal low-porosity “BSE-bright” calcite spar cement in pore spaces between “BSE-dark” micro-porous calcite bioclasts. Trace-element mapping of several areas (several mm² each) in each thin section by LA-quadrupole-ICP-MS reveals variably elevated Mn/Sr, U concentration, and U/Pb in the calcite spar cement. The trace-element maps were subsequently used to guide the placement of laser spots for U-Pb dating by LA-multicollector-ICP-MS. Primary bioclastic calcite in both samples has low U/Pb (²³⁸U/²⁰⁶Pb < 7) and, thus, does not yield precise Concordia-intercept dates. The primary calcite does, however, yield imprecise intercept dates within uncertainty of the depositional ages. Calcite spar cement has higher U/Pb (²³⁸U/²⁰⁶Pb up to ~15.7) and including all analyses, yields intercept dates of ca. 415 Ma in each sample. Additionally, several of the domains with the highest U/Pb from each sample yield slightly younger dates of ca. 400–380 Ma. The timing of calcite (re)crystallization and cementation identified here overlaps with the timing of continent collision during the Caledonian orogeny in Scandinavia. We tentatively interpret this to be a result of fluid flow in response to the collision far-inboard (>500 km) from the orogenic front. Furthermore, this work demonstrates that apparently

pristine carbonates may have experienced recrystallization (or at least chemical-isotopic perturbation) in open systems long after deposition.

References

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