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Quaternary spring-associated limestones of the Eastern Alps: implications for marine carbonates.

D. Sanders (1), R. Tessadri, (1), E. Rott (2)

(1) Faculty of Geo- and Atmospheric Sciences, University of Innsbruck, Austria, (2) Faculty of Biology, University of Innsbruck, Austria (Diethard.G.Sanders@uibk.ac.at)

In the Eastern Alps, deposits of spring-associated limestones (SAL) a few meters to about a kilometer in size are common. SAL deposition occurs when spring water sufficiently charged with Ca^{2+} and HCO_3^- equilibrates with atmospheric $p$$CO_2$, until kinetic equilibrium is attained by $CaCO_3$ precipitation. In the Alps, production of spring waters sufficiently supersaturated for $CaCO_3$ depends mainly on presence of sulfate evaporite and/or metal sulfides in subsurface rocks, combined with large faults enabling ascent of deep-sourced waters.

Eastern-Alpine SAL consist of tufa limestones and/or of massive laminated cementstones composed of fascicular-fibrous calcite, magnesian calcite, and aragonite that largely formed, and some still form, on the day-lit surface of streams shed from 'cool' springs. Eastern-Alpine SAL of late-Glacial to Holocene age are present between about 400 m to nearly 2600 m a.s.l., corresponding to a range in mean annual temperature between about 10˚C to below 0˚C, and a mean annual temperature gauge from 20-22˚ to 16˚C. Many SAL formed at sites with 5˚C to less than 0˚C present mean annual temperature consist of fascicular-fibrous calcite to magnesian calcite (up to 16 mol% $MgCO_3$) and/or of aragonite. Biogenic carbonate precipitation is induced by microbes, mainly diverse cyanobacteria and the green micro-alga *Oocardium*. Experimental precipitation in active SAL-depositing springs records microbially-induced carbonate laminae up to 10 mm thick per 6-8 months growth season. SAL are reminiscent to post-2.4 Ga Precambrian carbonates by (1) (microbial) biocalcification of induced type only, (2) lack of controlled biocalcification, and (3) formation of massive cementstones at the day-lit surface of the deposit.

Both in spring streams and in the shallow-marine realm, carbonate production is checked by atmospheric pCO_2. As modelled by other authors, because pCO_2 levels of the geological past were higher and fluctuating, the overall secular persistence of marine carbonate deposition must correlate with variations in Ca^{2+} and HCO_3^- concentration of sea water. Formation of fascicular-fibrous (magnesian) calcitic cementstones and/or of aragonite from Eastern-Alpine non-thermal spring waters, in surface environments with mean annual temperatures between 5°C to below 0°C, implies that the meaning of aragonite and magnesian calcite as indicators of a tropical-subtropical marine climate is to be questioned. Spring-associated limestones indicate that it is not 'climate' but water chemistry in feedback with atmospheric pCO_2 that steer carbonate precipitation and, to some extent, polymorphs formed in Earth surface environments. This calls for caution in the palaeo-environmental interpretation of marine carbonates of the distant geological past.