



New insights into biological influence on the geochemistry of freshwater carbonate deposits.

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Ambient temperature freshwater carbonates (“tufas”) have outstanding potential as palaeoclimatic archives, as they are composed primarily of carbonate, are seasonally laminated and accumulate extremely rapidly in regions frequently devoid of more conventional sources of palaeo-environmental records. Despite this potential, it has proven difficult to constrain the behaviour of the geochemical parameters that important proxy systems rely upon. Here, we provide evidence that though supersaturation is largely regulated by degassing, precipitation in natural tufas does not generally occur at the air-water interface. Rather, precipitation occurs at the bottom within benthic microbial communities (“biofilms”). When these communities are absent, precipitation occurs exclusively at the intersection of the air-water interface with a solid surface (i.e. the flume wall) and the bottom receives no significant carbonate flux. Furthermore, we report a series of experiments in which biofilm is shown to accumulate large inventories of calcium and other dissolved ions (Ba, Sr, Mg), and that this process is highly selective in favour of ions with low charge densities. These observations have consequences for interpretation of trace element records from tufas based on an assumption of equilibrium with river water, and also for other carbonate deposits associated with biofilm activity (travertines, marine stromatolites, lacustrine and soil carbonates, speleothems). Conversely, our study provides new insight into the reasons for discrepancy of tufa Mg/Ca ratios from expectation, and thus provides encouragement for the potential of Mg/Ca palaeothermometry in freshwater carbonate systems. The novel approach we describe provides a clear means by which this, and other, proxy systems can be calibrated.