

## Precipitation rate and isotopic composition of calcium carbonate under conditions induced by degassing of carbon dioxide

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It has been well known that degassing of carbon dioxide increases the saturation state and induces precipitation of calcium carbonate. Representative natural examples of this phenomenon are fluvial tufa in a limestone area, and travertine in carbonate hot-spring environments. These two examples largely differ in the precipitation rate. The difference is likely related with the differences in equilibrate partial pressure of carbon dioxide, alkalinity, and calcium concentration, however it has not been fully understand with a theoretical principle. In general, the carbonate precipitation has been treated as adjunction of carbonate and calcium ions on the mineral/water interface, which was often formulated by activity product of the two ions. The previous formulas are consistent with the rates in tufa environments, but fail to reproduce high precipitation rates of the travertines.

This study will propose a new rate formula based on the sum of chain-reactions, in which the degassing induces the carbonate precipitation. A prominent feature of this is that three ions (bicarbonate, hydroxide, and calcium) are captured on the mineral surface. The formulated rate is proportional to the product of the calcium carbonate saturation and the carbon dioxide partial pressure, and well reproduces the actual precipitation rates of tufas and travertines. In addition, the proposed model is consistent with an apparent disequilibrium of oxygen isotopic composition of travertine, which is variable with pH. The model can be more comprehensive than the previous ones in terms of reproducing the overall phenomena of carbonate precipitation.

Keywords: travertine, tufa