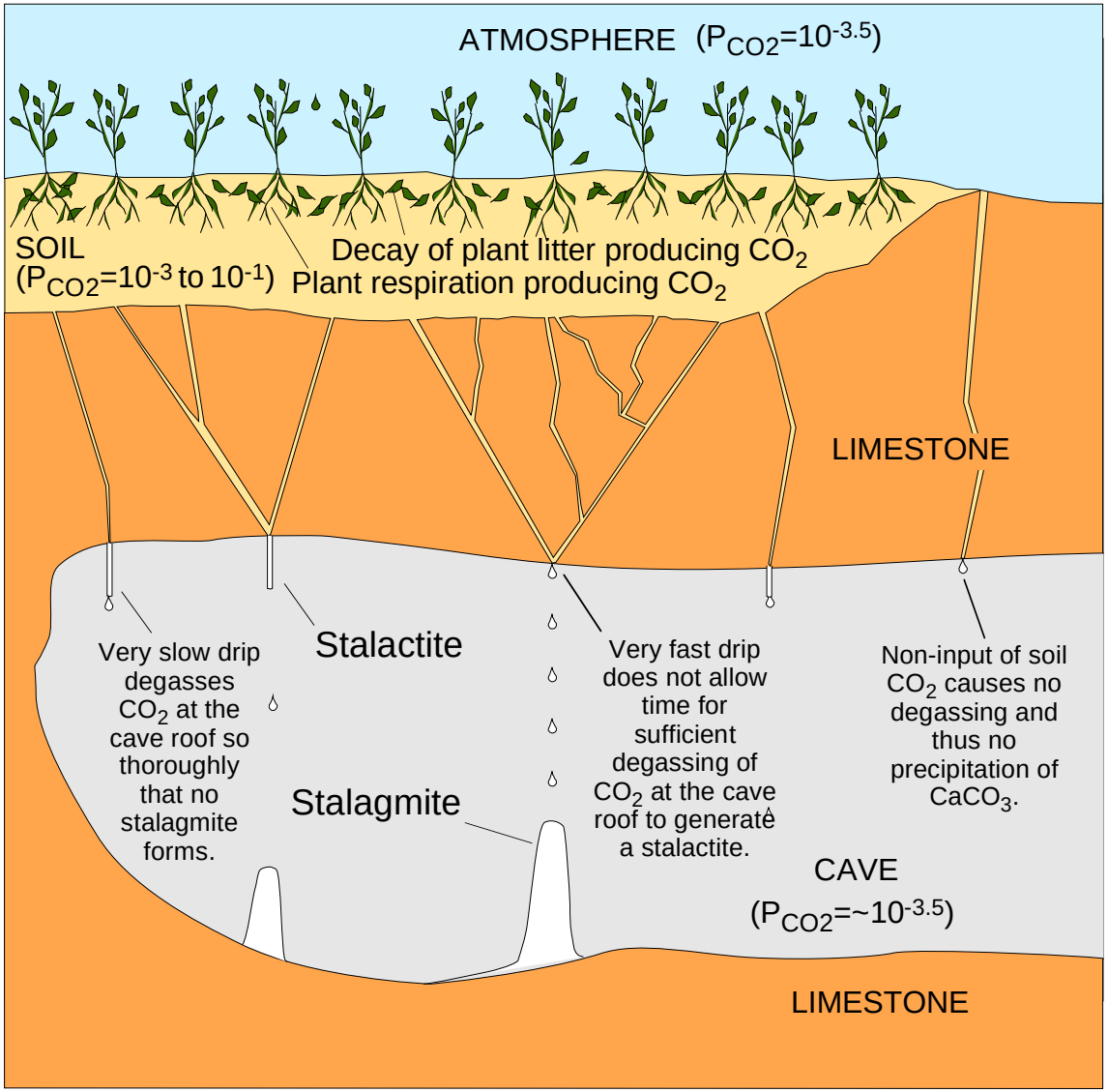
# Degassing of $CO_2$ in caves and precipitation of speleothems

Precipitation of $CaCO_3$ as speleothems can be driven by evaporation, which increases the $Ca^{2+}$ and/or $CO_3^{2-}$ concentration of the dripwater, or by degassing of $CO_2$ ,which increases the pH of the dripwater and thus increases the concentraton $CO_3^{2-}$. However, it is generally agreed that degassing is the more widespread mechanism, and it clearly must account for precipitation of $CaCO_3$ in cave settings in which relative humidity is 100% (which is typically the case). Degassing occurs because rainwater moving through soil is charged with $CO_2$ either by respiration in plant roots and/or by decay of plant matter. When this water enters the cave, it meets air with $P_{CO2}$ near that of the atmosphere and therefore degasses $CO_2$, causing supersaturation with respect to $CaCO_3$. The relationship between residence time of drips of water on the cave ceiling and time of that water to degas then determines whether only a stalactite forms (with a very slow drip), a stalactite and a stalagmite beneath form, or no stalactite forms (with a very fast drip).




*Dissolution of limestone calcite:*

Carbon dioxide from plant respiration or decay — Carbonic Acid

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2\,HCO_3^-$$

$H_2CO_3$: Carbonic Acid; $CaCO_3$: Calcite in limestone; $HCO_3^-$: Bicarbonate

*Precipitation of speleothems:*

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

$CaCO_3$: Calcite or aragonite in stalactite or stalagmite

$CO_2$: Degassing of carbon dioxide with entry to cave pulls reaction to right