Cave Air Ventilation and CO₂ Outgassing by Radon-222 Modelling: How fast do caves breathe?

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Introduction
Speleothems (stalagmites) grow their calcite paleoclimate records inside caves. Speleothem records of climate change can provide regional histories with annual resolution back many thousands to hundreds of thousands of years. To correctly relate ancient cave environments to overlying climate changes, it is essential to establish the micrometeorology and air & drip water chemistry of contemporary caves. The rate and timing of calcite precipitation (stalagmite growth) is governed by variations in cave air pCO₂ and calcite saturation state of the drip waters. We describe how a NW Florida preserve cave inhales and exhales CO₂, how the overlying seasonal climate changes (temperature, winds, rainfall) are transmitted downwards via soil gases and drip waters, and how drip water (soil) chemistry is translated into calcite dripstone (stalagmite) isotope and chemical compositions. The goal of this work is to establish quantitative relationships between long-term (decadal and century to millennial scale) regional temperature and rainfall changes to the oxygen and carbon isotopes incorporated into dripstone calcite, and the wet/dry climate influences of overlying soil water chemistry on drip water chemistry and isotopes incorporated into speleothems as a function of precipitation rates – transfer equations we call “paleoproxy calibrations of the present”. We are growing artificial speleothems (cave calcite farm) to test inferences drawn from the air and water chemistry.

Experimental
In October 2007 we instrumented micro-meteorological time-series stations inside and on top of Hollow Ridge Cave (HRC) in Marianna, FL, near the Florida State Caverns. Stalagmites extending back 70,000 years have been analyzed from caves in the area. Two stations inside the cave (one near and one far from the entrance) monitor these same parameters plus air ²²²Rn and CO₂ partial pressure. Occasional “snapshot” gas samples for cave air-¹³CO₂ and drip water chemistry are also obtained. A simple radon-222 air exchange model enables continuous mass balance solutions to the overall calcite drip-precipitation reaction:

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}. \]

Since cations, isotopes and dissolved-CO₂ (HCO₃⁻) are brought to the cave roof by dripping soil solutions with high pCO₂ and low pH, degassing of CO₂ inside the cave is a prerequisite for calcite precipitation and speleothem formation from roof drips. Thus caves must exhale CO₂ to form stalagmites. When and how caves breathe dictates how and when calcite forms.

Results and Discussion
Figure. Keeling plot of air grab transect May 2009, illustrating that HRC is a mixing & ventilation system with atmospheric and soilgas endmember sources of CO₂. The isotope composition of cave-air and thus calcite falls along this mixing line and is dependent on extent of ventilation.

Conclusions
Time series ventilation rates of CO₂ outgassing calibrated from a ²²²Rn air exchange model indicate that calcite precipitates in the winter during episodic periods of rapid ventilation. We predict that calcite δ¹³C in this cave monitors ventilation rates and not the C3 or C4 vegetation of the overlying canopy, the “standard” interpretation.

References