

The Geochemistry of Limestone Cave Waters: Implications for the Development of New Methods for Studying Paleoclimate

Kirstin Washington

Department of Earth and Environmental Science, University of Pennsylvania

Introduction

The chemistry of limestone cave waters tells an interesting and complicated story about the flow paths of water underground. The composition of cave water depends on interactions with soil air, cave air, and the rocks through which the water passes. The composition of cave water also depends on the kinetics of those interactions, which can vary due to factors like whether the water is still or flowing, the amount of water that is flowing at a given time, and the circulation patterns of the air in the cave.

Precipitation flows through soil and equilibrates with CO₂ rich air, becoming acidic. It then flows through and dissolves carbonate rocks. As it seeps through cracks in the cave, it encounters air with lower CO₂ concentrations and outgases, resulting in the formation of speleothems.

Methods:

To explore the chemistry of limestone cave waters, I collected water samples and conducted on-site measurements at Indian Echo Caverns, a commercial cave in Hummelstown, Pennsylvania, developed in Ordovician rocks. I measured the temperature and partial pressure of carbon dioxide of the cave air at different locations in the cave, and the temperature and pH of water in lakes, a spring, and water dripping from various speleothems. I performed laboratory titrations to determine the carbonate species present in water samples I collected; I used an Inductively Coupled Plasma instrument to find the concentrations of calcium and magnesium then calculated the bicarbonate concentrations; and I measured ¹³C/¹²C ratios using an Isotopic Ratio Mass Spectrometer.

Results

Sample Location	[Mg ²⁺] mmol/L	[Ca ²⁺] mmol/L	[HCO ₃ ⁻] mmol/L
Spring in Indian Ballroom	0.474	2.919	6.787
Mirror Lake	0.332	2.284	5.233
Fat Man's Misery	0.395	1.975	4.738
Rainbow Room	0.669	2.236	5.811
Crystal Lake Middle	0.992	2.425	6.834
Crystal Lake Back	0.970	2.375	6.689
Crystal Lake Front	0.793	1.880	5.346
Wedding Lake	0.903	2.181	6.166

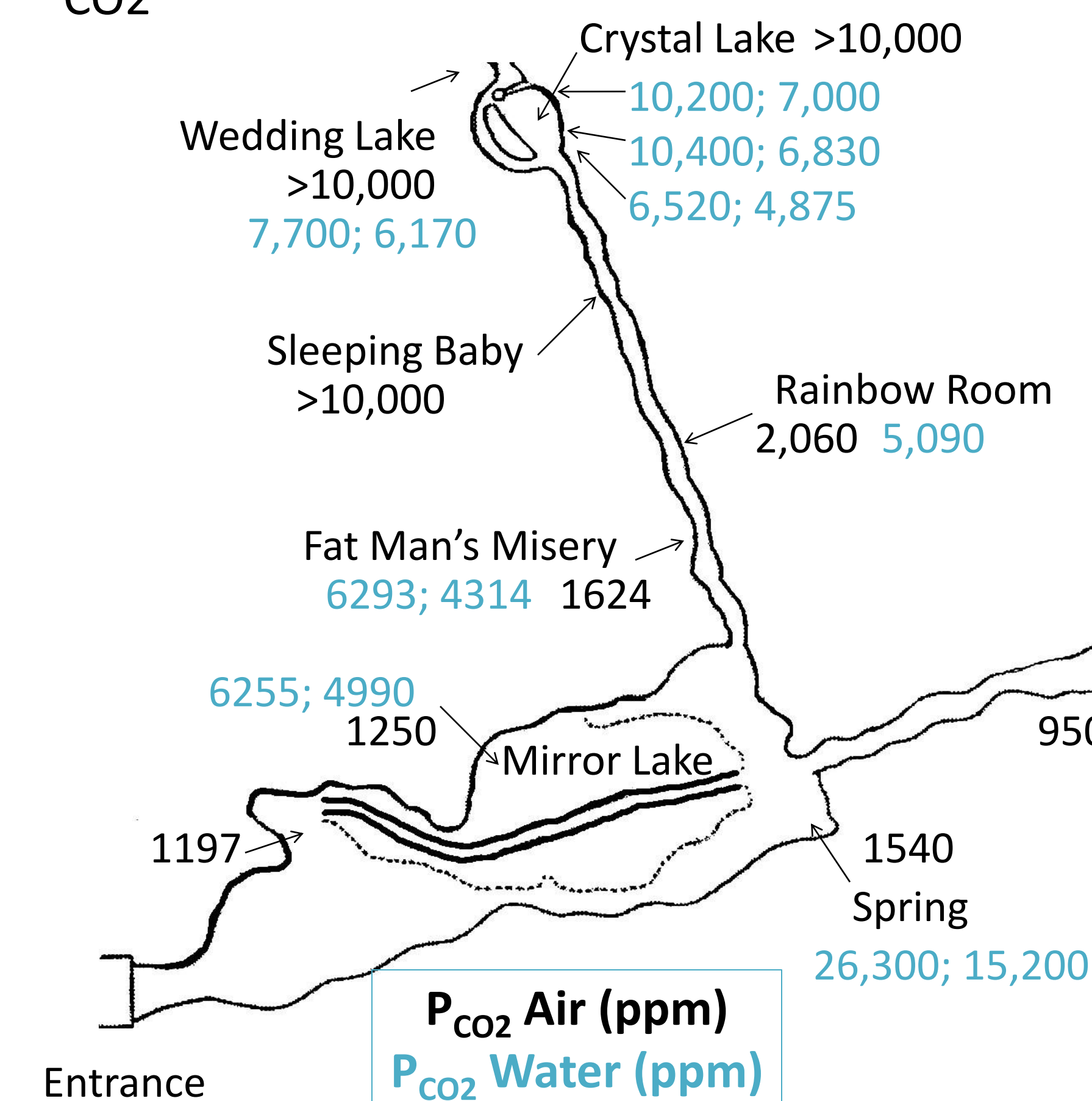
Magnesium, Calcium, and Calculated Bicarbonate ions in Solution



Mirror Lake

Indian Echo Caverns

P_{CO2} Values



¹³C/¹²C Ratios

Sample Location	δ ¹³ C/ ¹² C (‰)			
	A	B	C	D
Entrance Drip	-14.5	-11.1	-	-
Mirror Lake	-9.4	-3.8	-6.2	-6.1
Stream	-14.8	-10.5	-	-13.1
Fat Man's Misery	-9.2	-7.3	-	-7.1
Rainbow Room	-	-	-7.4	-
Sleeping Baby	-12.9	-9.3	-	-10.7
Crystal Lake Front	-10.9	-9.5	-6.6	-7.5
Crystal Lake Middle	-11.4	-	-10.9	-6.0
Crystal Lake Back	-8.5	-6.3	-7.4	-11.8
Crystal Lake Drip	-9.3	-	-	-
Wedding Lake	-	-	-4.1	-

Trials A: Large Vial B: Small Vial C: Bottle D: Small Vial

Discussion

The cave air P_{CO2} values elucidate the pattern of circulation and mixing in the cave. The pattern is expected due to the cave ventilation. The highest P_{CO2} levels occur at the deepest section of the cave, near Wedding Lake and Crystal Lake because it is relatively shut off from the rest of the cave and does not experience as much air flow as other portions.

The magnesium and calcium concentrations and the water P_{CO2} values reflect the expected outcomes based on the sample locations. Flowing water in the spring does not have enough time to outgas all of its dissolved CO₂, while lakes and slow drips are able to equilibrate with the cave air more easily.

While there is variation in the ¹³C/¹²C ratios at each location, their depleted nature indicates that the water holds on to the isotopic signature of the soil air and the cave. The soil air would have an isotopic ratio value ranging from -25‰ to -16‰ depending on the type of vegetation decaying in the soil, while the cave would have a value closer to 0‰. It seems likely that as the water equilibrates with the air, it picks up the signature of the air, which would be around -8‰ today.

In order to gain a better understanding of the trends in isotopic ratios, further sampling would be necessary.

Acknowledgements:

Thank you to Dr. Dick Holland and Dr. David Vann for helping me with the research and analysis process. A special thanks to the Swartz family of Indian Echo Caverns for allowing me to undertake the data collection.