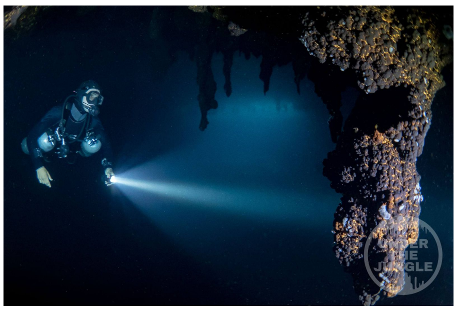
Under the Jungle - Geo Karst challenge - Sunday Sept 6

Colors in the caves!

COLORS in the cave walls and formations. Some caves are pure white, others are ivory or even golden. Is the color caused by minerals in the water, in the rock, in the soil? Are the colors in the rock itself or deposited onto the rock after? I have seen so many colors in the formations -- stalactites so black that light barely bounces off the walls, and even grays, oranges, and reds. Is it simple minerals that create these colors, or is something else going on – like the ash from surface fires that washes into the caves and makes the formations gray?



Our conversation today covered great distance and was wonderful to participate in. I am going to try and unpack this chicken/egg problem we are discussing: **Colors in the cave!**

What is the natural color of the rock?

The great majority of the Yucatan Peninsula rock goes from pure white to near orange, with mostly shades of cream. Quite a range.

Alot of the base color of the rock has to do with its depositional environment - was it originally fine grained sediment down in a shallow marine? Was it nice white beach sand? Does it include orange mangrove sediments? Is there surface soil that worked down with some red tropical soils coming with it?

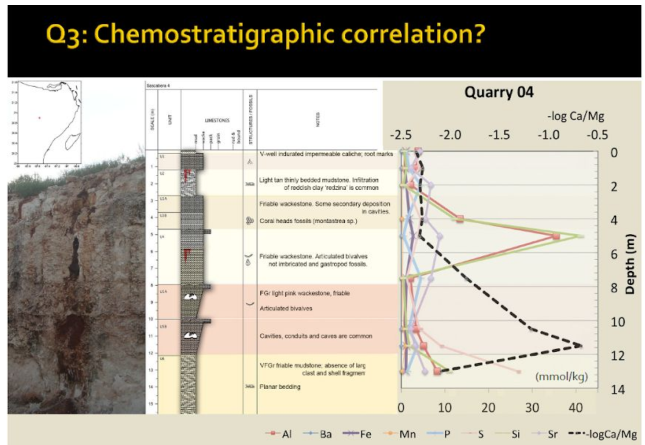
The tray of cut rock samples (ready for crushing to powder for chemical analysis) shows some of the range from the Caribbean side of the peninsula in near surface rocks.

When you go into quarries (and I *STRONGLY* encourage you to) you can see how the texture and colors change with depth (going down in time…). And - you can also see how the root holes and fractures allow for surface soils to work their way down making underground soil pockets.

In some places - the redzina is then cemented and lithified - turning it into a paleosol rock! (left slide - upper right).

And - the chemistry of the rock changes with the layers - from the original sediment and then also what happened to the rock after it was laid down.

Typically - the rock with more magnesium aka DOLOMITE - tends to be more glassy in texture and more grey (although the example in the slide here is still cream).



From - Monroy-Rios https://gsa.confex.com/gsa/2012AM/webprogram/Paper213256.html

What is the natural color of the speleothem?

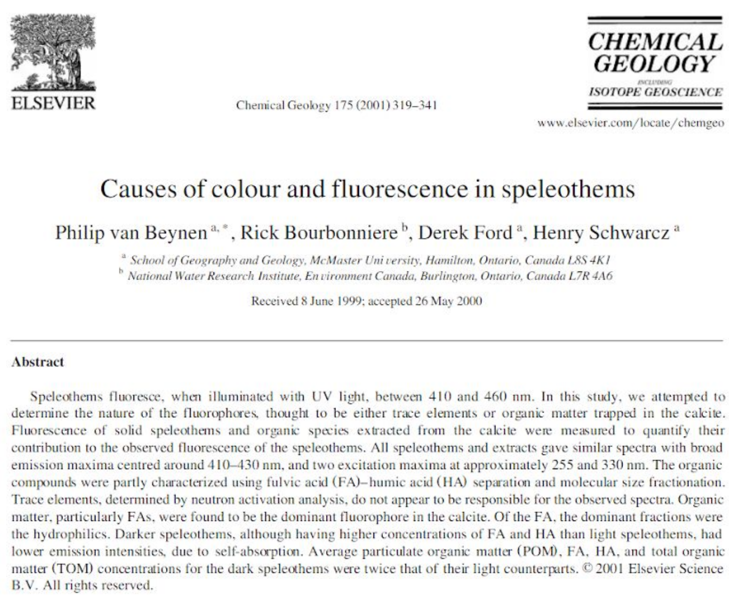
Where spleothem calcite forms in perfect conditions and especially with no dust or other particles, then they can be transparent. .

However - there is usually some dust and other particles, so the calcite is milky/opaque since it is a bunch of tiny small crystals due to the ïnterruptions”. With dust, the transparency is the first thing to be lost. If the dust is colorful, then the speleothem can then have the color of the dust - orange for tropical soils and grey/black for dark soils or even soot and smoke from fires.

However - as long as there are no particles in the formation water, then dissolved compounds can give color and you can still have transparent speleothems.

The infiltrating water flows through soil and decaying vegetation so inevitably picks up some orange/brown organic coloring (tannins - humic + fulvic acids) that leaches into the water. ***If*** the organic compounds survive to the drip point without being eaten by all the microbes….. Then the speleothems can have a huge range of colors from off-white to orange to pretty much black from the organic compounds in the infiltrating water.

Martin provided a key piece of science in our discussion - van Beynen et al - which was done in the lab when I was at McMaster actually doing my MS on the Nohoch Nah Chich system :-)


ELSEVIER Chemical Geology 175 (2001) 319–341

CHEMICAL GEOLOGY INCLUDING ISOTOPE GEOSCIENCE

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Causes of colour and fluorescence in speleothems

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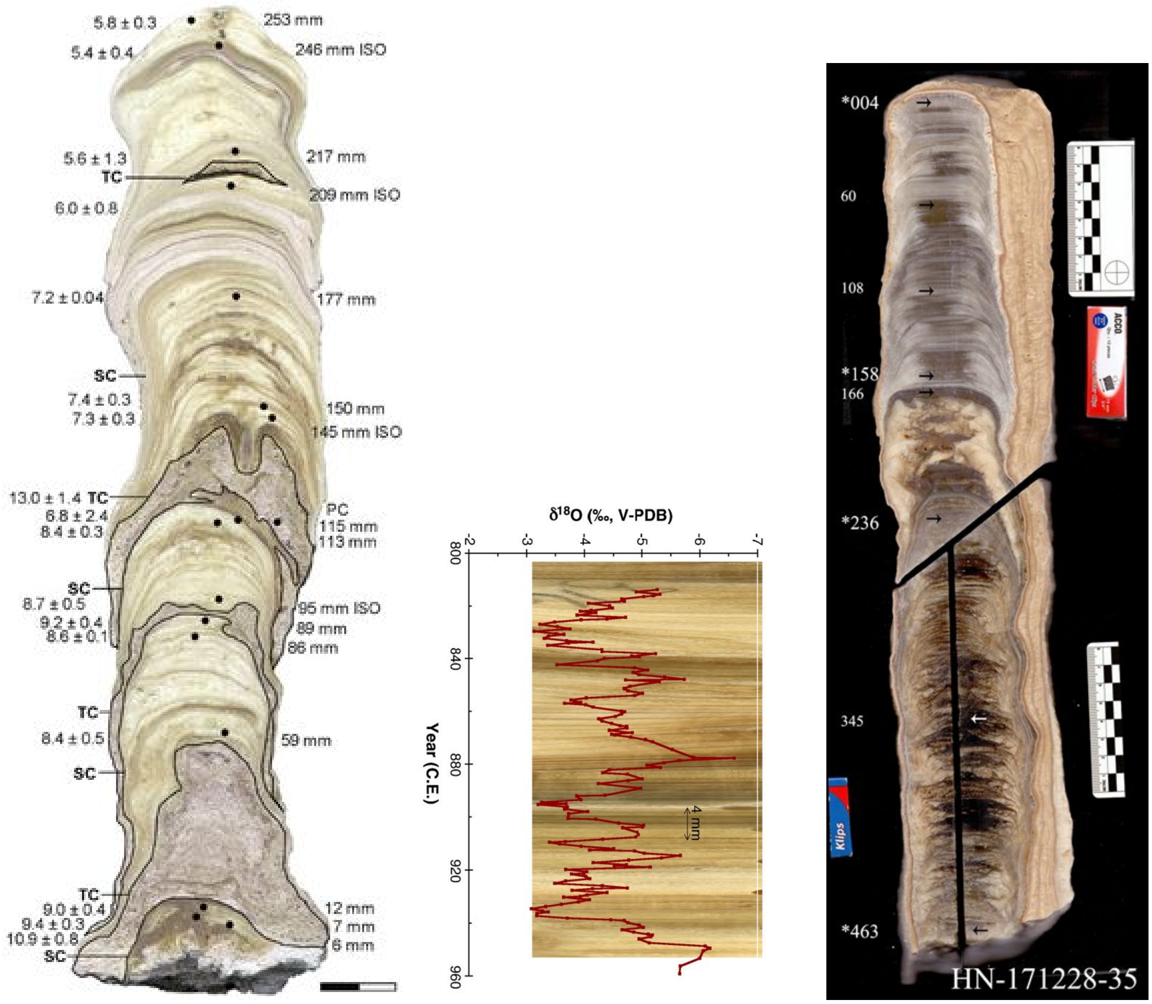
Received 8 June 1999; accepted 26 May 2000

Abstract

Speleothems fluoresce, when illuminated with UV light, between 410 and 460 nm. In this study, we attempted to determine the nature of the fluorophores, thought to be either trace elements or organic matter trapped in the calcite. Fluorescence of solid speleothems and organic species extracted from the calcite were measured to quantify their contribution to the observed fluorescence of the speleothems. All speleothems and extracts gave similar spectra with broad emission maxima centred around 410–430 nm, and two excitation maxima at approximately 255 and 330 nm. The organic compounds were partly characterized using fulvic acid (FA)–humic acid (HA) separation and molecular size fractionation. Trace elements, determined by neutron activation analysis, do not appear to be responsible for the observed spectra. Organic matter, particularly FAs, were found to be the dominant fluorophore in the calcite. Of the FA, the dominant fractions were the hydrophilics. Darker speleothems, although having higher concentrations of FA and HA than light speleothems, had lower emission intensities, due to self-absorption. Average particulate organic matter (POM), FA, HA, and total organic matter (TOM) concentrations for the dark speleothems were twice that of their light counterparts. © 2001 Elsevier Science B.V. All rights reserved.

Since that paper does not actually include color pictures! - Here are some pictures of actual Yucatan speleoethems -



First - Moseley et al 2015 https://journals.sagepub.com/doi/10.1177/0959683615585832 Second - thin and polished section - showing a close up of the color bands - Medina Elizalde et al 2010 - https://www.semanticscholar.org/paper/High-resolution-stalagmite-climate-record-from-the-Medina-Elizalde-Burns/f5457d73bece507cbe8cba640f870f6fbfd940a0 Third - unpublished new sample (Beddows collection - INAH project)

Can organic compounds from the forest / soil stain the cave wall and speleothems?

Oh heck yes. After the cave forms - and also after the speleothem forms - under the right conditions the organic tannins/humic+fulvic acids in the water can stain the rock and speleothems.

However - it does not always happen even when the water is highly colored and obviously requires the right conditions, or the right mix of organic compounds.

- The rock / speleothem has to be open enough “crystal”to take the stain. Rough surfaces with porous or previously etched surfaces ie from halocline dissolution - do seem to get stained more.
- There also has to be enough organic compounds in the infiltrating water. Therefore there has to be soil or forest above, and the compounds have to survive infiltratio (not all eaten by microbes).
- There has to be enough contact time - although again what constitutes long enough is poorly defined.
- We know broadly from the chemistry of dying tings (like hair or leather) that the right pH/redox/chelating agent which is often a metal is needed also to fix the dye. No- right now we do not have a good understanding of what fixes the organics but it is clear that some sites with highly colored water are not presently staining the wall noticeably.

When we see colorful bathtub rings on the walls of caves, I am left wondering if that is primary or secondary….. Is that ring that was formed and took up the coloring of the organic compounds that were at the water table at the time? That would be primary. Or - was that a ring that formed white and then got colored by the water some time later? That would be secondary. [systematic study is needed]

Here is an example of a “tannic”orange layer in Hoyo Negro - that happens to align with the depth of deposition of some of the major fossils. Initial analysis of the rock and coloring was unfortunately inconclusive and more work is needed. [scheduled for about now - but with COVID all in suspense.]

In alot of cases though - including in this example in Hoyo Negro - the color is quite superficial. Where the colored rock fallen off (or been broken off) the rock underneath is often VERY white - or at least a different color. Just like the individual layers in a speleothem can be VERY thin - the bathtub rings on the wall can be very thin too….

Alot of the color layers we see in the caves are over-printing - and secondary.

What is the thick scaly black stuff on some walls - for example in Jailhouse, or on all the walls in Crystal?

Right now - not well understood and I had a sampling transect with Bil Phillips going when he passed.

The best informed hypothesis - is that it is a manganese crust that in some way relates to the rock underneath and also the water.

Since you can swim along and find sections of passage with the crust well developed - but then hit a line where it stops - it does not look to be just the water chemistry alone. Indeed, the work of Monroy-Rios on the rock chemistry is showing great patchiness in the rock chemistry with some layers and areas having much higher iron, manganese and aluminum amongst other elements. (see section above).

We also know from other caves, and from surface sites, that the chemistry of the underlying rock - or the substrate - can control the formation of “desert rock varnish”and coloring rinds. Again Martin helped with a great example - with the rock substrate in Lascaux being a controlling factor.

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Rock substrate rather than black stain alterations drives microbial community structure in the passage of Lascaux Cave

Lise Alonso, Charline Creuzé-des-Châtelliers, Théo Trabac, Audrey Dubost, Yvan Moënne-Loccoz and Thomas Pommier

https://microbiomejournal.biomedcentral.com/track/pdf/10.1186/s40168-018-0599-9

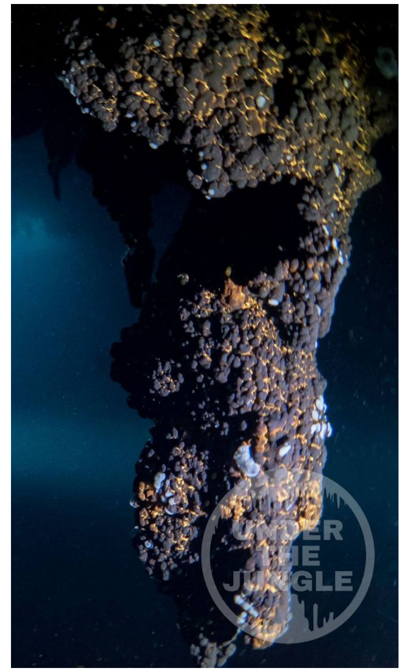
Overall though - microbes are super important

They are undoubtedly very important - although not always necessary.

For speleothem color - the microbes break down the organic matter above the cave allowing for the compounds to even be liberated to then flow down. At the same time - too much microbial action and there may not be any organic compounds left to color the speleothem. Goldilocks conditions needed.

Where microbes grow in colonies on the rock - often in patches - they locally without question create colonies that precipitate minerals and crusts.

Nat’s picture really looks like a speleothem formation that was likely stained orange, and then has colonies growing on the nubbly bits that have more flow over them. Since this picture is shallow and near a cenote - they probably benefit from having plenty of organic material in the water to mineralize.

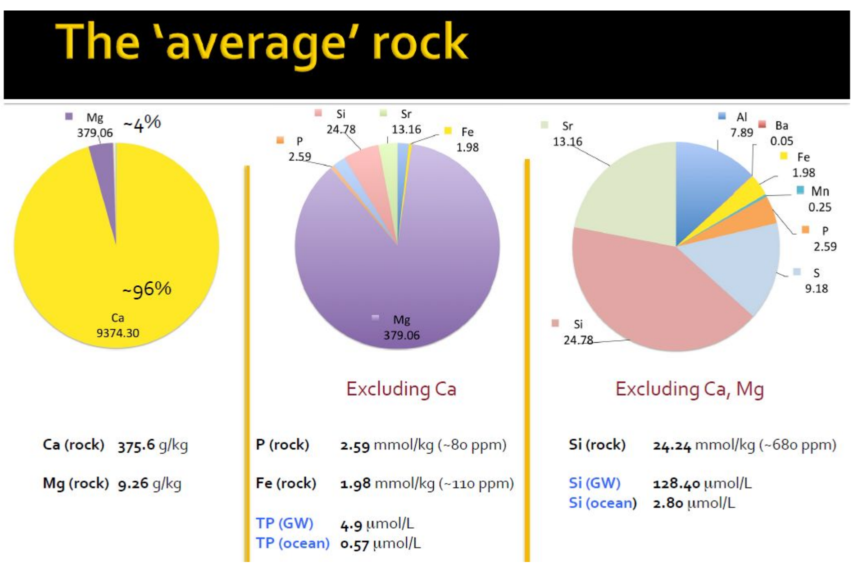


I am convinced that we see many of these interesting and striking “rinds”where there is the specific combination of mineral availability from the rock substrate ANd the microbes.

Here is a snapshot of the bulk rock chemical composition of some 400 rock samples to show the ”average” rock (Monroy-Rios work again).

The calcium and magnesium are nearly 100% of the rock - and once you take those out - There is a mix of everything else…. But really these are very small concentrations of the total.

There is not much to work with really - so powerful microbial action that is good for concentrating scarce elements is needed - and undoubtedly at play - especially where water is flowing “fresh” water over a surface for the microbes to harvest from.



A special case may be the combination of S and iron to form pyrite H2S ….. Especially in the halocline in sites with little water flow.

Iron is limited - but we know we have abundant dissolved sulfur in the density interfaces - particularly where surface organic material is broken down microbially.

I have one example of rapid pyrite formation with even some elemental sulfur (yellow precipitate).... But the sample was re-dissolved away in the water before it could be captured.

For me the biggest unknown for the black rinds is manganese crusts - similar to desert polishes that form in surface sites. TBD - maybe next year we know more.