Unearthing the sources of cave-forming sulfuric acid

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Dimitri Laurent explores a typical gallery in the Nébélé Cave, which was formed by sulfuric acid speleogenesis. You can see a deep notch that indicates the former presence of a river, and sodium sulfate on the left that is produced from weathering by sulfuric acid. Credit: Christophe Durlet

A study published in the journal *Geology* uses isotopes of sulfur to fingerprint the sources of sulfuric acid that have carved unique and beautiful cave systems in the Pyrenees mountains of southern France.

Networks of caves form when carbonate rocks like limestone dissolve. These are also known as karsts. In most caves, water has trickled down through Earth's surface, picking up carbon dioxide and becoming slightly acidic along the way; this is the same type of mild carbonic acid that you'll find in a can of soda that has carbon dioxide dissolved in it.

A rarer type of cave forms from transport of fluids up through the crust and through fault zones, forming vertical caves that can connect with horizontal caverns, forming large networks. In some cases, when sulfur is present, sulfuric acid forms and acts to dissolve limestone much faster—forming caves 10–100 times faster than its carbonic acid counterparts.

When sulfur compounds are present in water or in the minerals in the cave walls, chemical-loving bacteria use the sulfate as an energy source, producing hydrogen sulfide as a by-product. Oxidation of this hydrogen sulfide then forms sulfuric acid. Sulfuric acid can also come from hydrothermal springs or from minerals within the rock, and both are true in the northern Pyrenees.

Sulfur comes in four different isotopes—each weighing a slightly different amount. Researchers were able to estimate the relative contributions of sulfuric acid from different sources by using these isotopes as a marker of where the sulfur originated.

The large network of limestone caves in the foothills of the French Pyrenees mountains was formed by a combination of acid-forming processes that left their imprint on the minerals left behind. Sulfur-containing minerals like gypsum and mirabilite in the caves hinted that sulfuric acid was involved in their formation. Mirabilite is a rare mineral that forms long, thin crystals up to 50 cm in length that radiate out like flowers.

Rare large mirabilite crystals (sodium sulfate) up to 50 cm long observed in the Nébélé Cave provide a fingerprint of the sulfur isotopes left behind by sulfuric acid weathering of the limestone within which the caves formed. The length of the photo is 1 meter. Credit: Dimitri Laurent

For the first time, researchers studying limestone caves carved out by sulfuric acid have estimated how much of the cave-forming acid was produced by bacteria within the cave versus how much was produced by thermochemical processes. This innovation in separating the various sources of limestone dissolution has also allowed them to make the first estimate of how much carbon dioxide was emitted by the formation of

the caves.

Dimitri Laurent, lead author of this study, explains, "We tried to identify hydrothermal springs close to measured faults, and then we contacted the local speleological clubs to visit the caves near the springs. We see that at depth in the Northern Pyrenees, in the northern foothills, there are Triassic evaporites that produced hydrogen sulfide through thermochemical processes 65 million years ago."

That hydrogen sulfide then traveled through fractures in the rock and has been trapped within the cave host rock since then. As water began to dissolve this sulfur-rich rock, the fossil hydrogen sulfide was liberated and oxidized to form sulfuric acid. The Triassic evaporites have also delivered sulfates to the caves more recently, via deep hydrothermal fluids, which are then used by bacteria within the cave.

Combining chemistry with physical observations of the landscape, the researchers reconstructed the history of how these spectacular caves came to be.

More information: D. Laurent et al, Unravelling biotic versus abiotic processes in the development of large sulfuric-acid karsts, *Geology* (2023). DOI: 10.1130/G50658.1

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