



A Sulfuric Acid Speleogenesis in the northern Pyrenees? Example of the Arbailles karstic region (West Pyrenees, France)

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The polyphasic tectonic evolution of the northern Pyrenees (southern France) makes the context of foothills a privileged place for deep fluid circulations. Among these, the presence of CO₂- and H₂S-rich deep brines has been identified in the South-Aquitaine oil & gas fields, trapped within Jurassic and Cretaceous carbonate formations. Expelled from the depths to the margins of sedimentary basins, H₂S is likely to form large cavities in the carbonate host rock when it interacts with O₂ to form sulfuric acid (H₂SO₄). Known to be an important “cave-forming agent” in various places around the world, this Sulfuric Acid Speleogenesis (SAS) has never been proven in the Pyrenees through concordant morphological and geochemical data.

The exploration of numerous caves along the north-Pyrenean foothill has revealed several evidences of this hypogene speleogenesis, particularly in the Arbailles region (Pyrénées-Atlantiques, France). In this massif, several karsts developed in the Cretaceous and Jurassic carbonates show morphological markers (deep notches, convection niches, replacement pockets, ceiling channels and cupolas) and minerals (gypsum, sulfides, hydrothermal carbonates) compatible with the action of the SAS. These karstic networks are notably located close to thermo-mineral springs containing abnormal concentrations in dissolved sulfates and sulfides.

In addition to field observations, petrographic and mineralogical analyses, coupled with isotopes geochemistry (carbon, oxygen and sulfur), allow to reconstruct the paragenetic sequences during dissolution/precipitation phases affecting the karstic systems and to decipher the sulfur cycle involved in the speleogenesis. The comparison of sulfur isotopic signatures between cave sulfates and all the potential sources of sulfur at the scale of the Arbailles basin (Triassic evaporites, pyrites and pyrrhotites in sedimentary formations, dissolved sulfates and H₂S from thermo-mineral springs) indicates that the precipitation of gypsum in karst results from the oxidation of H₂S, confirming that the SAS has played a role in the development of some cavities. The production of sulfuric acid occurred during the interaction between meteoric waters and ascending H₂S which, according to the multiple sulfur isotopes, derived from the thermochemical reduction of the Triassic evaporites at depth. Then, the fabric of H₂S-rich carbonate veins affecting the karsts, whose carbon and oxygen isotopic signatures confirm the thermochemical reduction, specifies that the H₂S migration started during the Cretaceous extension. A part of this H₂S is even still adsorbed in the Jurassic rocks today. However, for the time being, we do not have solid arguments on the true timing of the SAS, which may be either contemporary with the production of H₂S during Cretaceous or more recent link to the oxidation by meteoric water of the H₂S previously adsorbed in the host rocks.

Understanding the functioning of hypogene karsts is crucial, especially concerning the exploration of geothermal resources, but also the engineering/environmental hazards related to the impact of per ascensum fluids in the formation of large vertical void-conduit systems and leakages of H₂S.

Keywords: Sulfuric Acid Speleogenesis, hypogene karst, Pyrenees, structural geology, fluid-rock interactions, sulfur isotopes.