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New insights on the coloration causes of green and blue speleothems from two French caves

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Cave speleothems are usually white to brown when composed of calcium carbonate. However, several natural or anthropogenic processes can produce a wide variety of colorations in these remarkable geological structures. These processes can be diverse and include the presence of metallic elements in substitution, foreign colored minerals, humic or fulvic acids, or microbial communities. In previous studies, we discussed the causes of green speleothem coloration in the Aven du Marcou (Hérault, France) [1] and of blue speleothem coloration in Malaval Cave (Lozère, France) [2]. Here, we present a set of new, unpublished results aimed at refining our understanding of the various processes leading to speleothem coloration.

Green speleothems in the Aven du Marcou are characterized by the presence of nepouite, a green, Ni-bearing phyllosilicate, in the outer parts of the speleothems. The Ni in nepouite most likely originates from the overlying rocks, which contain Ni-rich pyrites. EPMA results suggested that this nepouite is unusually enriched in Zn, allowing us to propose a structural formula for the Marcou nepouite $[(Ni_{1.63-2.43}Mg_{0.20-0.44}Zn_{0.00-0.61})Si_{2.06-2.26}O_5(OH)_4]$. New analyses, including LA-ICP-MS, provide a more extensive and better spatially and spectrally resolved chemical characterization of the nepouite, making it possible to refine the previously calculated structural formula.

Blue speleothems in Malaval Cave are primarily characterized by the presence of Cu^{2+} in substitution within aragonite, producing a generally desaturated blue coloration. In some samples, however, Pb^{2+} substitution was also detected and, in some cases, correlates with a more saturated blue to greenish coloration within the aragonite lattice. More specifically, the 30 cm-long blue stalactite that we were able to sample exhibits several color variations, with a strong correlation between the presence of Pb and green coloration. Here, we present unpublished XPS, ToF-SIMS, and PIXE results that provide new insights into this phenomenon, including a better understanding of chemical variations achieved through spatially resolved Cu, Zn, and Pb compositional profiles.

1. Vlieghe, M. et al. Ni-rich mineral nepouite explains the exceptional green color of speleothems. Sci. Rep. 13, 1–8 (2023).

2. Vlieghe, M. et al. Polymetallic interactions of Zn-Pb-Cu in blue/green-colored speleothems from Malaval Cave (France). Geochemistry 85, 126285 (2025).



