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Sulfuric Acid Speleogenesis in Italy: geomorphological, mineralogical and geochemical evidences

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Italy hosts $\sim$ 25% of the known worldwide sulfuric acid speleogenetic (SAS) systems, i.e. very peculiar caves linked to the upwelling of acidic sulfidic waters, able to corrode carbonates and create important underground environments. SAS caves have been observed and documented, especially, along the Apennine chain, but also in Apulia, Sicily and Sardinia and some of them are still active and host microbial mats similar to those found in Cueva de Villa Luz (Mexico). The most famous and well-studied systems are La Grotta and Faggeto Tondo in Monte Cucco, Umbria, where SAS processes are no longer active, and Acquasanta Terme and Frasassi in the Marche region in which sulfidic waters still rise into the cave. SAS caves present characteristic morphologies like cupola-like structures, domes, replacement pockets, feeders, pendants, megascallops related to acidic rising water and/or vapor fluxes. These fluids are enriched with H2S, which in oxidative environments, transforms into H2SO4, immediately replacing the carbonate host-rock producing gypsum (CaSO4•2H_2O) and CO_2 as the major endproducts. Nevertheless, other minerals can abundantly be formed, in such conditions, in particular native sulfur (S0), celestine (SrSO4), but also typical hypogene hydrothermal materials such as alunite (KAl3(SO4)2(OH)6), natroalunite (NaAl3(SO4)2(OH)6), and jarosite (KFe3+(SO4)2(OH)6). Using scanning electron microscope, we analyzed several of the previous described deposits and discovered that they are often enriched in PO4, which might reflect the source of parent solutions. Barite (BaSO4)-fluorite (CaF2) have been found in assemblage in Monte Cucco caves, suggesting processes similar to those at the origin of Mississippi Valley ore deposits to have been active at some stage during their development. Significant authigenic needles and spheres of Ti-rich minerals like rutile (TiO_2), ilmenite (Fe2+TiO_3), titanite (CaTi(SiO4)O), due to H2SO4 digestion, have been observed both in Cavallone-Bove and in Monte Cucco systems. The finding of these peculiar mineralogical associations together with geomorphological evidences, give new insights on the genesis of fifteen Italian SAS systems, some of which were not known to be hypogenic caves before, such as the fossil SAS caves of Cavallone-Bove (Majella Massif), and the much smaller Acqua Mintina and Grotta che Parla caves in Sicily. In addition, the presence of active systems, nowadays used as thermal spas (Porretta Terme, Santa Cesarea Terme, Cassano allo Ionio and Cerchiara di Calabria) allowed us to monitor environmental parameters, to make field measurements of limestone- and gypsum tablet weight loss, and to collect water samples from several sulfidic springs during different seasons to understand more about the dissolving action of the rising waters and vapors in and above the water level, and their sometimes complex and variable geochemistry. SAS caves represent interesting systems that deserve to be deeply-studied, showing significant clues about their origin and helping to elucidate the steps of landscape evolution of the area in which they formed. Still active SAS caves are also interesting natural laboratories to learn more about extremophile, and often chemioautotrophic, microorganisms, and how these interact with the hostrock and are involved in the formation of secondary mineral deposits and speleogenesis.