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Raman spectroscopy in the study of hydrothermal cave minerals: Implications for research on Mars

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Regarding that the ExoMars mission of the ESA, scheduled for launch in 2018 will be equipped with a Raman spectrometer, investigations by Raman spectroscopy on Earth's minerals are essential to interpret data coming from this further mission to Mars. Among terrestrial minerals, cave minerals represent an opportunity to better understand the genesis of Martian minerals and the evolution of Mars itself, in particular by studying minerals formed in hydrothermal conditions, as well as those generated due to hydrothermal alteration of previous materials. The absence of solar radiation, practically constant temperature at daily and seasonal scale and the presence of liquid water are some of the attractions which make caves interesting for Martian research.

In the present work, we have studied a great variety of cave minerals from hypogenic/thermal mine-caves like the Giant Geode of Pulpí (south-eastern Spain), the caves of the Naica mine (northern Mexico), the caves of the San Giovanni Mountain (Sardinia, Italy) and Baume Galinière Cave (south-eastern France). Carbonate, sulphate, sulphurs and polymetallic oxyhydroxides are the most common minerals found in these cavities. Among them, it is worth noting the presence of several minerals of the jarosite group and gypsum, since these minerals have been recently discovered on the Mars surface. Both of them are hydrated minerals, which genetic mechanisms are linked to the presence of liquid water. In the case of jarosite minerals, identification of species like argentojarosite and plumbojarosite confers worth to the Raman technique against other methodologies, like XRD by which the characterization of the jarosite group minerals is difficult.

As a consequence of the recent discovery of Ca-rich sulphates (probably gypsum) on the surface of Mars, attention has been focused on the terrestrial gypsiferous formations. The gypsum samples from the Giant Geode of Pulpí and the caves of the Naica mine, which are subject of this work, displayed low fluorescence background and thin-shaped Raman signals that suggest high purity and crystallinity. On the basis of these evidences, we propose gypsum speleothems from the Naica caves and the Giant geode of Pulpí to be included in the mineral spectroscopy database for Mars exploration as reference materials.

Furthermore, Raman signals related to the presence of organic compounds, particularly oxalates, have been found mainly in polymetallic oxyhydroxides like birnessite, sometimes as solid inclusion in gypsum and carbonate. Identification of these features is not possible by using other mineralogical techniques such as XRD. Thus, the Raman spectroscopy is a powerful tool that complements other techniques, for instance IR spectroscopy, for studying evidences of life on the surface of Mars. Such results have an important astrobiological significance, since these cave minerals formed without the influence of solar radiation. In conclusion, Earth's caves offer a wide range of features which could be studied as potential Martian analogues.

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