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Sulfur and oxygen isotope constraints on the genesis of gypsum in caves from Cerna Valley (Romania)

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Cerna Valley in SW Romania is famous for its thermal springs, which have been known since Roman times. The Baile Herculane Spa is located in the lower part of the Cerna Valley, right above an important positive geothermal anomaly. Thermal gradients of the anomaly are 6 fold higher than the average normal value. Many springs have high contents of H_2S and SO_4^{2-} ($>$ 76 mg/l and $>$ 90 mg/l, respectively), their temperature reaches 58 ºC, and native sulfur is precipitated around them.

Two of the main structural units of the area, i.e., The Cerna Graben and the Cerna Syncline are the major karst hydrogeological features. A number of caves that cluster in the walls along the Cerna Gorge are known to host significant gypsum deposits. The morphology of caves from Cerna Valley reflects the geological, structural, and hydrogeological settings under which they developed. The presence of hydrogen sulfide-rich thermal waters along Cerna Valley, argues for the hypogene origin of these caves (formed by oxidation of hydrogen sulfide to sulfuric acid and reaction of the latter with limestone). Massive gypsum deposits (crusts, blocks, and crystals), corrosion features (cupolas, pendants, blind ascending galleries), and anastomotic passages are typical for cavities developed in the mixture zone between ascending hydrogen sulfide-rich solutions and oxygen-rich, descending meteoric waters. The present study intends to discriminate the origin of gypsum based on isotope (sulfur and oxygen), geochemical and mineralogical analyses. Based on our preliminary data, the gypsum from the Barzoni Cave shows to be dominantly hypogene in origin with heavy sulfur and oxygen isotopic compositions ($d^{34}S$ (SO_4) = -14 – -17 permil and $d^{18}O$ (SO_4) = 0.2 – 2.3 permil.