Raman spectra on Fluid Inclusions in Glauberite from Miocene saline lakes of the Madrid Basin: evidence for microbial activity.

M.E. Sanz-Montero[1], L. González-Acebrón[2]; J.P. Rodríguez-Aranda[1] & C.P. Marshall[3]

1 Dpto. Petrología y Geoquímica. Fac. CC. Geológicas (UCM). IGE-CSIC. C/ José Antonio Novais, 2. 28040 Madrid, Spain.
2 Dpto. Estratigrafía. Fac. CC. Geológicas (UCM). IGE-CSIC. C/ José Antonio Novais, 2. 28040 Madrid, Spain.
3 Department of Geology, University of Kansas, Lawrence, KS 66045-7613, USA

Glauberite ($Na_2Ca(SO_4)_2$) layers occur interbedded with magnesitic marlstone and evaporites (mostly halite and anhydrite) in the Madrid Basin, Central Spain. These rocks were deposited in a saline lake-mudflat sedimentary system during the Lower Miocene. The Ca-Na sulfate generally occurs as intrasedimentary crystals, although contorted or nodular beds are also observed. Glauberite consists of euhedral to subhedral hemipyramidal crystals which in some beds are tightly cemented by cubic halite precipitates. Glauberite crystals show both fluid and fluorescent solid inclusions of the host magnesitic marls. Magnesite precipitation has been interpreted to be mediated by microbial activity. Although glauberite is a common sulfate in inland evaporitic basins, its origin continues to be a matter of debate. Primary fluid inclusions in glauberite are analysed in this study in order to get more information in the formation of the mineral and to elucidate the possible role of microorganisms in the precipitation processes. Primary fluid inclusions (related to growth zones) have been recognized in this glauberite in oil-prepared thin sections from a core. Fluid inclusion assemblages (2 and 40 µm) are formed by very variable liquid: vapour ratio fluid inclusions (10/90 to 60/40), including all-liquid and all-gas fluid inclusions, which is characteristic of a low-temperature heterogeneous entrapment. An attempt to measure the final melting of ice temperature (in order to obtain the salinity conditions of formation) has been done in a Linkam stage, but no results have been obtained because the sample degrades upon freezing. To our knowledge, no salinity data from glauberite inclusions has been collected, probably due to the delicate nature of this mineral. Thus, Raman microprobe provided an adequate alternative to obtain the main components present in the fluid inclusion assemblages. Raman analysis of the samples was performed on a XRD confocal Raman Thermo Fischer Microscope in the MNCN, Madrid. Excitation was provided by the 532 nm line of a diode laser. Zones of primary fluid inclusions have been studied preferentially; nevertheless, spectral signatures of the glauberite host mineral have been examined as well. Glauberite presents its characteristic spectral features with mean bands at 1150, 998, 648, 470, 449 cm^{-1} and the presence of broad features attributed to hydrocarbons, between 1615 and 1440 cm^{-1}. These features assigned to hydrocarbons became more important in the fluid inclusions, in which the glauberite signature is weaker. In fluid inclusions, complex Raman spectra in the C-Hx stretching modes (2700-3000cm^{-1}) are observed which can be attributed to diversity of CH, CH_2 and CH_3 groups. A 1440 cm^{-1} band is assigned to bending CH_2 modes. Bands from 3000-3100 cm^{-1} are aromatic C-H stretching modes. A mode at 1610 cm^{-1} is an aromatic C=C stretching mode. The spectral signatures of the fluid inclusions reveal also the presence of N_2 (2320 cm^{-1}), O_2 (1550 cm^{-1}), CO_2 (1370 and 1290cm^{-1}), SO_2 (1150 cm^{-1}) and COS (842 cm^{-1}). The inclusion of liquid hydrocarbons and organic-rich compounds in fluids would be indicative of microbial communities in the matrix embedding the sulfate crystals. Therefore, the microorganisms and the organic compounds may have favoured the precipitation of glauberite.

Additional work is being undertaken to determine the type of organic matter included in the minerals by resonance Raman spectroscopy.