# Application of Raman spectroscopy to study the $CO_2$ dissolution kinetics in water and the growth of $CO_2$ hydrate

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Raman scattering of dissolved $CO_2$ in aqueous solutions (pure water and seawater) allowed us to study the transport properties and mass transfer of liquid or gaseous $CO_2$ across the phase boundary into the water. Therefore, a new high-pressure cell, suitable for Raman spectroscopy, was designed hosting a water-filled glass capillary. The phase behavior of the $CO_2$ was controlled by the applied pressure. The uptake of $CO_2$ into the water phase was recorded in high spectral resolution: Over time, the peak intensity of the Fermi dyad doublet of dissolved $CO_2$ increased until the aqueous solution was saturated with respect to $CO_2$. Measurements were carried out at various pressures and temperatures within and outside the hydrate stability field. The measurements allowed us to determine the mass transfer coefficient of $CO_2$ across the gas-liquid and liquid-liquid boundary as well as the growth rate of gas hydrate formation.

$CO_2$ hydrates crystallize in a sI-type cubic structure composed of polyhedral water cages occupied by the guest molecule carbon dioxide. The Raman spectra of $CO_2$ hydrates and the surrounding $CO_2$ gas/liquid were obtained by moving the laser spot across the hydrate skin at the interface. Two large peaks at 1275 $cm^{-1}$ and 1381 $cm^{-1}$, that are characteristic for the $CO_2$ molecule in the hydrate phase, were observed. Two strong Raman modes and two satellites are observed in the gas/liquid phase, respectively at 1285 $cm^{-1}$ and 1388 $cm^{-1}$ (first Fermi dyad) and 1265 $cm^{-1}$ and 1409 $cm^{-1}$ (second Fermi dyad). Finally, numerical transport-reaction modelling was applied to interpret the $CO_2$ concentrations derived in time and space from the Raman microscopy.

# Mineral magnetic studies on the intrabasaltic bole beds from the Deccan Volcanic Province, India

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The intrabasaltic red and green bole horizons along with respective underlying and overlying basalts from Pune and Rajahmundry areas of the Deccan Traps were analyzed for routine mineral magnetic studies from 10 sampling sites. The results indicate significant variations in the magnetic susceptibility for the red bole samples (2-3 times the underlying basalts) and green bole samples (1/5$^{th}$ of the underlying basalts) from the Pune area. On the contrary the susceptibilities for red and green boles from Rajahmundry area are about 1/100$^{th}$ times lower than the respective underlying basalts. This indicates entirely different environment or mechanism for the formation of bole beds in these two widely separated areas. Further there is a significant contribution of $\chi_{fd}$% (>10%) in the red boles and negligible $\chi_{fd}$% for green boles from Pune area and red & green boles from Rajahmundry area. This suggests a significant presence of super paramagnetic fractions during the Pune red bole formation that may be of volcanic dust-aerosol origin. The remnant coercivity ($B_{CR}$) for the Pune red boles varies between 30 to 60 mT indicating majority of single domain ferromagnetic grains as compared to the values of 20 to 32 mT from the Pune green boles indicating soft ferromagnetic (multi domain or pseudo single domain) contribution of detrital origin. On the contrary the Rajahmundry red boles show very high $B_{CR}$ (of the order of ~ 180 mT) indicating dominant antiferromagnetic minerals of hematite-goethite composition while Rajahmundry green boles show $B_{CR}$ ~ 60 mT. Overall the present study infers that the formational set up for all these bole beds is of varied nature i.e. Pune red boles having formed under sub-aerial (oxidizing) conditions; Pune green boles under sub-aqueous (less oxidizing) conditions; Rajahmundry red boles under sub-aerial (highly oxidizing) conditions and Rajahmundry green boles having formed under sub-aqueous conditions with significant detritus derived from highly oxidizing provenance.