QUANTITATIVE RAMAN SPECTROSCOPY (QRS), A POTENTIAL TOOL TO STUDY THE FORMATION MECHANISM OF CARBONATES OF EARLY EARTH AND MARS.
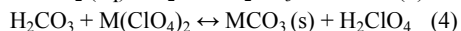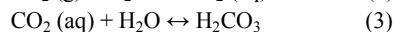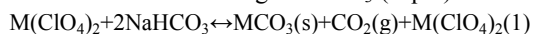
L. J. Bonales[1, 2], M. V. Muñoz-Iglesias[1], M. Sanchez-Román[1], D. Fernandez-Remolar[1] and O. Prieto-Ballesteros[1] . [1]Centro de Astrobiología. INTA-CSIC. Torrejón de Ardoz, 28850 Madrid. Spain, [2]Departamento de Química Física I, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain. (bonales@cab.inta-csic.es)

Introduction: Carbonates form an important mineral group for astrobiological/geological studies, since they (1) can directly or indirectly be the result of microbial metabolic processes, (2) are very common in Earth´s geological record, and (3) can remove C from the planetary biogeochemical cycle. Calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] are the two most abundant carbonate minerals on Earth. This is consistent with equilibrium thermodynamic considerations for the environmental conditions under which most sedimentary carbonate minerals form and persist [1].

In the present study, we focus on the abiotic formation of carbonates and we show that QRS is a good tool to get new insights about their mechanism of formation. Our findings are of fundamental importance for understanding modern environments in which carbonate minerals form as a window into the geologic past, and can explain how their formation can affect the biogeochemical cycles of other planets like Mars.

Materials and Methods: Reactants were purchased from Sigma-Aldrich. Raman spectra were excited with a 532 nm line of an solid laser at power 200 mW. After passing a monochromator (Horiba JobinY-von HRi 550) the scattered light was detected with a CCD. *High Pressure Planetary Environment Chamber* is a facility of Centro de Astrobiologia (Madrid, Spain), and consists of a stainless steel high pressure cell. It has a control temperature system and four ports for making different "in situ" analysis.

Results: Carbonate synthesis can be performed using two-ways. First, formation of MCO_3 from bicarbonate (Eq.1) and second, from $CO_2(g)$, which once is solubilized to $CO_2(aq)$ (Eq.2) and protonated (Eq.3) can react with free M^{2+} to give MCO_3 (Eq. 4).

$$M(ClO_4)_2 + 2NaHCO_3 \leftrightarrow MCO_3(s) + CO_2(g) + M(ClO_4)_2 \quad (1)$$
$$CO_2(g) + H_2O \leftrightarrow CO_2(aq) \quad (2)$$
$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \quad (3)$$
$$H_2CO_3 + M(ClO_4)_2 \leftrightarrow MCO_3(s) + H_2ClO_4 \quad (4)$$

where M means Ca, Mg, Fe, Mn, Ba, and/or Sr. These reactions are governed by the concentration of M^{2+} in the medium and several parameters such as pressure (P), temperature (T), ionic strength and pH. The first method can be studied measuring the decreasing in concentration of the bicarbonate ion, while the second one can be analyzed by measuring the solubility of CO_2 (Eq. 2) (Note that the Eq. 2 is the limiting step in the second method). We highlight QRS as a tool to analyze the kinetic of these reactions.

QRS analysis of HCO_3^-: The vibrational spectra (lattice and internal modes) of hydrogen-carbonate in aqueous solution were carried out over a wide range of concentrations (0.01-0.1M), taking into account the concentration of CO_3^{2-} formed by autoprotolysis of HCO_3^-. The HCO_3^- and CO_3^{2-} activities in each solution were determined using the software PHREEQC [2]. The relationship between the calculated HCO_3^- and CO_3^{2-} activities, and the relative area of the most intense bands in the Raman spectra allows us to calculate the activity of HCO_3^- at any time in the Eq. 1, and, therefore the amount of MCO_3 formed as a function of time, T, P and pH.

QRS analysis of $CO_2(aq)$: We performed a systematic study of the aqueous CO_2 in pure water (Eq. 1) at different T and P by using Raman spectroscopy. The vibrational spectra of the gas-water mixture at equilibrium were performed at certain conditions of T and P from which the solubility of CO_2 in water is well know. The existence of an isobestic point in water allows normalizing all the obtained spectra at different physical conditions. We obtained a calibration curve for the $CO_2(aq)$ based on the relative Raman area of the dominate peak of the spectra and the theoretical solubility of CO_2 at each condition. From this calibration curve, it is possible to calculate the amount of $CO_2(aq)$ during the formation process (Eq. 2), and consequently the amount of MCO_3 precipitated at different conditions of T, P and ionic strength.

This study can help to clarify paradigms from the early Earth and Mars environments. We simulate the formation conditions of some ancient carbonates assuming: a) the atmosphere contains high concentration in CO_2 during Hadean-Archean, therefore we use the second method (Eq. 2, 3 and 4) at T >20ºC and P up to 300bar; b) there were some global glacial crisis during Proterozoic, so for this aim we will study the first synthesis method (Eq. 1) at <0ºC and P up to 50bar.

References: [1] Morse and McKenzie (1990) Geochemisty of sedimentary carbonates. Developments in Sedimentology, 48. Elsevier, New York. 707 pp.[2] Parkhust and Appelo (1999): User´s guide to PHREEQC (V.2) – a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259. USGS, Denver, CO.