

## Raman monitoring of carbonate dissolution/precipitation in a CO<sub>2</sub> atmosphere at high pressure. Planetological applications.

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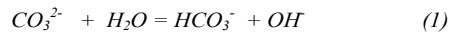
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### Abstract

Laboratory experiments on CO<sub>2</sub> solubility at high pressure in already carbonated solutions are performed. Processes of dissolution/precipitation of the mineral species are monitored by raman spectroscopy. pH is measured in situ during the solubility processes with a novel reflectance sensor. Carbonate minerals are planetologically relevant mainly because they play a role in the C biogeochemical cycle in potential habitable environments. The resulting data may be applied to understand the occurrence of carbonates on Mars and other objects of the solar system.

### 1. Introduction

The equilibrium involving hydrogencarbonate (HCO<sub>3</sub><sup>2-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) species in aqueous solution have been studied extensively at atmospheric pressure due to their important role in the earth, planetary and life science.



However, the experimental studies of these species at high pressures, specially the effect of the gases diluted such as CO<sub>2</sub> (aq) in these aqueous solutions are scarce.

In this work, we present Raman spectroscopy and pH measurements of different solutions of carbonates, and/or sulfates, in presence and absence of CO<sub>2</sub> gas as temperature decreases.

### 2. Methodology

For these experiments we have developed a high pressure chamber, HPPSC, (high pressure Planetary Simulation Chamber). The chamber has two windows which allow us to do Raman spectroscopy and pH measurements in situ.

Raman spectra were excited with a 532 nm line of a solid state laser at power 200 mW. After passing a monochromator (Horiba JobinYvon HRi 550), with three diffraction gratings: 1200, 1800 and 2400 grooves/mm), the scattered light was detected with a Charged Couple Device, (CCD). The spectrometer and laser are connected to an optical probe head trough fiber optical cables, (100 μm and 50μm) respectively.

The pH sensor system (Ocean Optics) consists in a fiber optic probe designed to measure the different color of a colorimetric indicator dye (in contact with the aqueous solution) by reflectance spectroscopy.

The experiments have been performed preparing the studied solution at room temperature and housed inside the HPPEC; the CO<sub>2</sub> (g) at the chosen pressure is injected, and then we decrease the temperature. At each temperature of analysis, the system was kept isothermal during at least 12 hours as stabilization time and raman spectra and pH data are taken from the supernadant.

### 3. Results and Discussion

In Fig.1 is showed the molal concentrations of hydrogencarbonate (HCO<sub>3</sub><sup>2-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) in absence (pH= 11) and presence (pH= 6) of an

atmosphere of 50 bar of  $\text{CO}_2$  (g) as the temperature decreases.

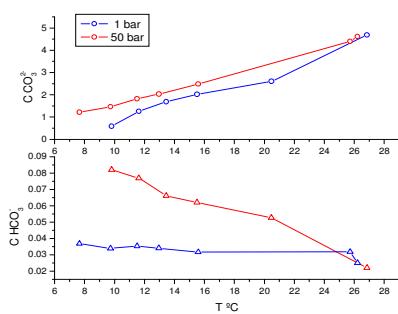


Figure 1: Molal concentrations of hydrogencarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) species in aqueous solution as a function of temperature at different pressure

As can be observed, the concentration of carbonate decreases with the drop of temperature, in both cases as expected. The concentration of hydrogencarbonate in absence of  $\text{CO}_2$  remain constant whereas in presence of  $\text{CO}_2$  increases. This behaviour highlight the great effect of the  $\text{CO}_2$  and then of the pH at the equilibrium of the hydrogencarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) species i.e. when the  $\text{CO}_2$  at high pressure is present, the pH decreases dramatically (from pH 11 to pH 6) and it gives rise to a displacement of the equilibrium towards acid species, ( $\text{HCO}_3^-$ ).

Carbonates have been detected in some planetary objects of the solar system, apart from the Earth. They are present in several meteorites [1,2]. Also they have been recently observed by remote sensing [3, 4] and in situ by rovers [5] in different areas of Mars. All of them seem to be associated to hydrothermalism activity. In the case of Mars, they are controversial because more extensive layers could be predicted depending on the acidity of the supposed aqueous reservoirs on the surface in early times. During that ancient period, the atmosphere was thicker, thus acidic conditions produced by the  $\text{CO}_2$  injection may cause the dissolution of the minerals, as predicted by our experiments.

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