

CALCITE FORMATION FROM NANOPOROUS AMORPHOUS SILICATES IN INTERACTION WITH CARBON DIOXYDE. J. Gillot¹, M. Roskosz¹, C. Depecker¹, P. Roussel² and H. Leroux¹, ¹Laboratoire de Structures et Propriétés de l'Etat Solide UMR 8008 CNRS USTL 59655 Villeneuve d'Ascq, France (jessy.gillot@ed.univ-lille1.fr), ²Unité de Catalyse et de Chimie du Solide, UMR 8181, CNRS USTL 59655 Villeneuve d'Ascq, France

Introduction: Carbonates have been recently detected in dust shells of evolved stars [1] and protostars [2,3] suggesting that they could form under dry conditions (without liquid water). Around young stars, silicates are mainly magnesium-rich, amorphous and porous dusts [4], believed to form in the interstellar medium (ISM) by irradiation [5]. Such material is far from equilibrium and potentially highly reactive. In addition, their small size and their porosity should enhance their reactivity. More specifically, such material should undergo extensive transformations during gas-grain interaction that occurred in the nebula. Here we study experimentally the direct formation of carbonates from an amorphous and nanoporous Mg-Ca-rich silicate exposed to carbon dioxide rich atmosphere.

Experiments: Amorphous and nanoporous diopside ($\text{CaMgSi}_2\text{O}_6$) was first synthesized by acid sol-gel route using a nitrate based sol-gel method developed in our laboratory [6]. In this method, nitrate salts, used as magnesium and calcium carriers, are first diluted in solvents. Subsequently, they are mixed with a source of silicon oxide (TEOS) in acidic conditions to gently polymerize a silica network embedding homogeneously other cations. A monophasic and clear gel is then obtained. Finally, the gel is aged, dried and annealed to burn impurities and by-products to get a pure amorphous silicate. Composition, homogeneity and porosity of this precursor material were checked by transmission electron microscopy (TEM) and electron dispersive spectroscopy (EDS). A fluffy structure of nanoclusters stuck together and exhibiting a high open porosity is observed (pore diameter is 50-100 nm). The composition is relatively homogeneous at a 100-nanometer scale with a Mg/Ca ratio close to 1.

After its synthesis, the precursor material was ground in an agate mortar. Interaction with gas was performed by *ex-situ* and *in-situ* experiments. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and X-Ray Diffraction (XRD) were both used to track any transformation of the silicate material. Concerning *ex-situ* DRIFTS experiments, the precursor material was stored in air and regularly analyzed. These conditions correspond to a CO_2 partial pressure of about 0.35 mbar and an average H_2O partial pressure of about 3 mbar. In *in-situ* DRIFTS experiments, spectra were continuously recorded on samples enclosed in an environmental

cell under continuous flux of carbon dioxide. Finally, *in-situ* XRD experiments were carried on. Carbon dioxide was flown in a Guiné-Lenné diffraction chamber furnace. First, samples are rapidly heated up to 600°C in order to burn carbonates already present and that formed at ambient temperature. Then, they are cooled down to 50°C and carbon dioxide is fluxed at atmospheric pressure. A diffraction film records the process to determine time required for carbonate formation.

Results: DRIFTS reveals that precursor material shows typical features of amorphous silicate (i.e. the broad bands at 500 cm^{-1} and 1000 cm^{-1} on fig. 1). As expected for sol-gel materials, the water and -OH absorption bands are still significant (broad bands between $\sim 2200\text{ cm}^{-1}$ and $\sim 3700\text{ cm}^{-1}$). The region around 1500 cm^{-1} is a complex combination of carbonates and water vibration bands. But its broad shape suggests that water bands are overdrawn. Nevertheless, after exposure to air for 7 days, a new band (Fig. 1) corresponding to the most intense absorption band of standard CaCO_3 appears at $\sim 1400\text{ cm}^{-1}$. It is of note that the intensity of this band increases with the residence time of the sample in air (Fig. 1). This suggests that the material reacts easily with atmospheric carbon dioxide.

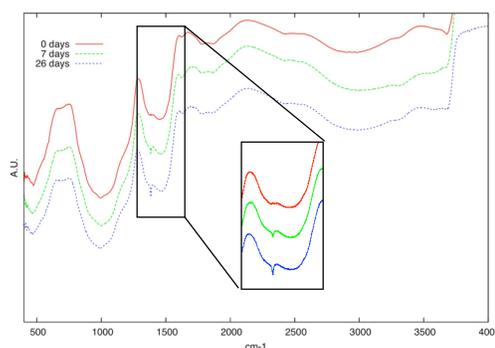
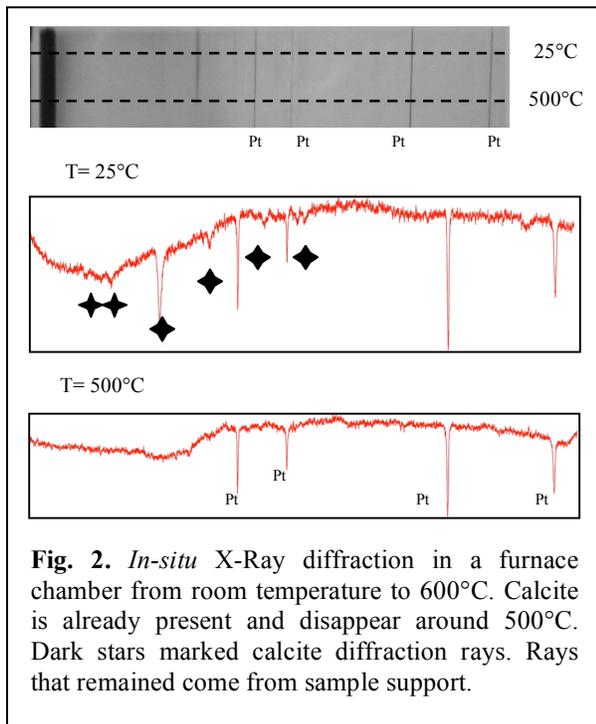


Fig. 1. DRIFTS evolution of the carbonates absorption band at $\sim 1400\text{ cm}^{-1}$ in amorphous diopside stored in air at room temperature. Band intensity increases with exposure time.

In-situ X-ray experiments confirm the presence of carbonates. Samples previously stored in air were heated from room temperature to 1200°C (Fig. 2). At room temperature, few broad bands are observed. They can be attributed to calcite CaCO_3 (Fig. 2) and their broadness argues for a highly disordered or partly amorphous structure of the carbonates. Subsequently, these bands disappear when temperature increases and no crystalline signal is collected anymore at temperature higher than 500°C. Other *in-situ* experiments are currently in progress to understand the mechanisms and the kinetics of the carbonation/decarbonation reactions of the amorphous parent silicate.



Discussion: Experimental direct condensation of hydrated carbonates from a mixture of a solar gas and $\text{CO}_2 + \text{H}_2\text{O}$ gases has been recently reported to explain the presence of carbonates in dust shells [7]. Surface alteration of dust grains with gases is an alternative proposed mechanism [1] to explain presence of calcite in dusts. However, despite the fact that thermodynamic calculations show that dry carbonation of forsterite, enstatite or diopside by CO_2 (partial pressure <1 bar) at low temperature (<300 K) is energetically favorable, kinetics are extremely slow [8]. This makes this formation process difficult in a protoplanetary disk.

Our results indicate that the amorphous state of the parent silicate dust favors the carbonation reaction. This contrasted behavior between crystalline

and amorphous material was consistent with a previous study that showed that carbonation of anorthite glass is faster than the crystalline counterpart [8]. Moreover, the formation of intermediate species such as hydroxide $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ were also experimentally observed [9], suggesting that hydrated minerals are more reactive than nominally-anhydrous minerals. Since our precursor material contains a lot of $-\text{OH}$ species, they can participate to the calcite formation.

This experimental study demonstrates that magnesium- and calcium-rich silicate dust observed in the ISM and injected into protostellar disks are particularly reactive with CO_2 even at relatively low partial pressure and low temperature. Its amorphous structure and its high ratio surface/volume probably counterbalance the high activation energy responsible for the extremely slow kinetics of the reaction. Furthermore, if these grains are slightly hydrated (or hydroxylated), the carbonation may even be faster.

Even if dry carbonation of crystalline silicates with gaseous CO_2 is slow at room temperature [8], these preliminary results show that carbonation in astrophysical environments is easily amenable with amorphous dust analogs and under relevant conditions of pressure, temperature and timescale. Our study confirms that a dry surface interaction is a viable mechanism to form carbonates observed in stellar environments. Further work is however needed to check that such reaction can occur on strictly anhydrous starting material or if a low amount of hydroxyl groups in the solid, and/or water vapor in the gas phase are required.

References: [1] Kemper F. et al. (2000) *Nature* 415, 295-297. [2] Ceccarelli C. et al. (2002) *A&A* 395, L29-L33. [3] Chiavassa A. et al. 2005 *A&A* 432, 547-557. [4] Demyk K. et al. (2000) *ISO beyond the peaks, The 2nd ISO workshop on analytical spectroscopy*, 456, 183-186. [5] Demyk K. et al. (2001) *A&A*, 368, L29-L33. [6] Gillot J. et al. (2009), *To Be Submitted*. [7] Toppani A. et al. (2005) *Nature* 437, 1121-1124. [8] Lackner K. S. et al. (1995) *Energy* 20, 1153-1170. [9] Zevenhove R. et al. (2006) *Catalysis Today* 115, 73-79.