

Experimental evidence for condensation of "astrophysical" carbonate. A. Toppani^{1,2*}, F. Robert², G. Libourel^{1,3}, P. de Donato⁴, O. Barrès⁴, L. d'Hendecourt⁵, J. Ghanbaja⁶, ¹Centre de Recherches Pétrographiques et Géochemiques, Nancy, France, ²Muséum National d'Histoire Naturelle, Paris, France, ³Ecole Nationale Supérieure de Géologie, Nancy, ⁴Laboratoire Environnement et Minéralurgie (LEM), Nancy, ⁵Institut d'Astrophysique Spatiale (IAS), Orsay, France, ⁶Université Henri Poincaré (UHP), Nancy, *current address: IGPP, Lawrence Livermore National Laboratory, Livermore, USA, toppani2@llnl.gov.

Introduction: The observation of the ~91 μm band in infrared spectra of two planetary nebulae [1] and one protostar [2] has been recently attributed to the presence of carbonates. Because of the absence of large parent bodies in these environments, such carbonates could not have been formed by aqueous alteration. The common association of carbonates with liquid water has thus been questioned. However, these detections remain controversial [3]. Furthermore, the only known mechanism to form carbonates at low pressure (1 bar) is aqueous alteration. An experimental study has thus been conducted to understand the possibility to form carbonates without liquid-water. The main dust component observed in these astrophysical environments is amorphous silicate [4], which is thought to have condensed far from equilibrium [5]. Here, we report the first experimental evidence that carbonates can be formed in association with amorphous silicates during non-equilibrium condensation in circumstellar conditions.

Experimental: Our design [6] consists of a reaction chamber linked to a high-vacuum metal line in which different mixtures of gases can flow. In the reaction chamber, the multi-elemental refractory gas to be condensed is produced by laser ablation (Nd-Yag laser) of a glass target of known composition. We previously showed [4] that the produced gas is not fractionated relative to the target. The ablated glasses were close to "solar" composition [7] for calcium, aluminum, magnesium and silicon (MgO, SiO₂, Al₂O₃, CaO: 36.1, 56.9, 4, 3 wt%), or of Ca-Al rich composition (MgO, SiO₂, Al₂O₃, CaO: 9.3, 48.6, 18.7, 23.4 wt%). Condensation of these refractory gases was performed in static vacuum mode at different total pressures (from 0,001 to 30 mbar) of different mixtures of gases (Ar, CO₂, H₂O+CO₂). Temperatures of these ambient gases, i.e. condensation temperatures were varied between 25°C and ~150°C, and condensation times from ~40 to 464 min. The condensed material was collected on a horizontal steel plate 2 to 10 cm above the target.

Condensed material was studied by transmission electron microscopy performed at UHP. It was analyzed in the mid-infrared (4000-600 cm^{-1}) by micro-Fourier Transform InfraRed spectroscopy at LEM and in far-infrared (700-50 cm^{-1}) at IAS.

Results: Condensed material collected during these experiments (ambient gases CO₂, Ar ~4 mbar or H₂O+CO₂ ~25 mbar) consist of fluffy ~10 nm size particles. Indeed, during laser ablation, the hot laser-ablated gas expanding in the cold ambient gas is rapidly supersaturated due to the relatively high pressure in the reaction chamber, which leads to the non-equilibrium homogeneous condensation of nanoparticles above the target [8]. TEM observations of the nanoparticles have shown that they are not chemically fractionated ($\pm 20\%$) relative to the gas composition and that they are amorphous in almost all explored conditions.

As shown by Fig.1, the infrared signatures of the condensed material are different depending on the nature of the ambient gas. Products condensed in "dry" CO₂ or Ar gas (sample 119) show spectra characterized by the stretching mode of Si-O-Si vibrators (980-1000 cm^{-1}) whereas spectra of material condensed in "wet" CO₂ (H₂O + CO₂) gas from Ca-Al-rich or "solar" gas (sample 130) show, in addition to the Si-O-Si vibrations feature (1), three new features. Features (2) and (3) correspond to H₂O bending (~1600 cm^{-1}) and stretching (~3300 cm^{-1}) vibrations. Their shape suggests the presence of highly bonded water and trapped free water. Feature (4), in the 1500-1320 cm^{-1} region is assigned to the carbonate doubly degenerate asymmetric stretching ν_3 [9]. The presence of highly bonded water, the splitting of ν_3 into two main components (~1430, ~1360 cm^{-1}) and the position of these components suggest the existence of complex hydrated carbonates [10] with site distortions and several crystallographic distinct CO₃²⁻ groups in the structure. The presence of carbonate is also noticeable in the far-infrared spectrum of material condensed from Ca-Al-rich gas (25°C, 493 min) in "wet" CO₂ (20 mbar H₂O + 4 mbar CO₂) since the spectrum shows bands at 318, 227 and 110 cm^{-1} , similar to calcite lattice vibrations [9].

Mid and far infrared spectra of Ca-Al-rich or of "solar" condensates indicate the presence of calcium-rich carbonates within the amorphous silicate matrix. Electron energy loss spectroscopy showed that the repartition of these condensed carbonates within the matrix is not homogeneous. Using integrated absorption coefficients of 100-300 $\text{cm}^2\cdot\text{g}^{-1}$ for ν_3 and 1500-3000 $\text{cm}^2\cdot\text{g}^{-1}$ for the Si-O-Si band (1020 cm^{-1}),

the relative amount of carbonate is ~ 1 to 10 % for both condensates. Annealing experiments of samples condensed in wet CO₂ (e.g. annealing of sample 130 in 0,001 bar of Ar at 65°C during 10 days) yield compaction of the nanoparticles and crystallization of Ca-rich nano-domains, whose diffraction patterns indicate the crystallization of Ca-rich carbonates from the amorphous ones.

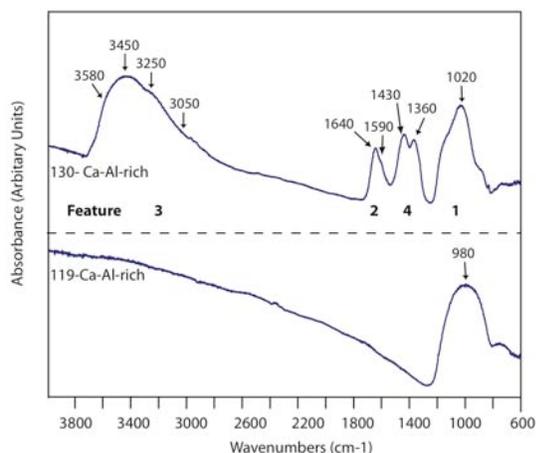


Figure 1: Mid-infrared spectra of material condensed from Ca-Al-rich gas either in 4 mbar of dry CO₂ ambient gas during 42 min (sample 119) or in a mixing of 4 mbar of CO₂ and 20 mbar of H₂O during 55 min (sample 130).

Discussions: As (i) several months air exposure of the samples condensed in "dry" CO₂ does not yield any formation of carbonate and (ii) the structure of the carbonate depends on the condensation conditions, formation of carbonates outside the apparatus by alteration in air can be ruled out. In addition, because carbonates still form when partial pressure of water is much lower than the equilibrium vapour pressure, they cannot be formed in the reaction chamber by surface reaction between liquid water (deposited as molecular layers of H₂O) and the nanoparticles. Indeed, the evolution of the amount and structure of carbonate, highly-bonded water and silicate with P_{CO₂}, P_{H₂O} and temperature suggests the implication of a kinetically controlled chemical reaction in the formation of carbonate, P_{H₂O} being the limiting parameter. We propose that the reaction proceeds in two steps: (1) hydration in the gas phase of molecular clusters of Ca or Mg-rich silicate and (2) reaction of these complexes with CO₂(g). Such a reaction would occur during the non-equilibrium condensation of the amorphous silicate nanoparticles.

In the planetary nebula NGC6302, NGC6537 and in the protostar IRAS4, water vapor and CO₂ are likely present [11, 12, 13]. Furthermore, shock-waves yielding high super-saturation levels required to favor non-equilibrium condensation probably occur. We thus propose that the detected carbonates could have

been formed by chemical reaction between H₂O, CO₂ and silicate gas during non-equilibrium condensation. Such a process would produce carbonate to silicate ratios close to those observed in both environments [1, 2]. It would also explain the presence of amorphous silicates and the observed ~91 μm (110 cm⁻¹) infrared band, which can be attributed to amorphous carbonates rather than to crystalline material (Fig. 2).

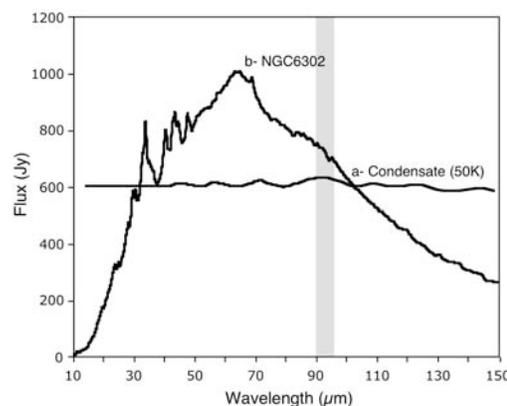


Figure 2: (a) Infrared signature of material condensed at 25°C in 20 mbar H₂O-4 mbar CO₂ during 493 min. Its expected emission at 50K has been obtained by multiplying the absorbance spectrum by a Planck function at 50K. The ~92 μm band of the NGC6302 planetary nebulae spectrum (b) is well fitted by the carbonate band of the amorphous condensates.

Conclusion: These experiments show, for the first time, that it is possible to form carbonates using only gas phase species. This mode of carbonate formation by non-equilibrium condensation may be widespread in circumstellar environments where water vapour is ubiquitous [14]. The future detection of extraterrestrial carbonates in astrophysical environments will no longer directly imply the presence of liquid water.

References: [1] Kemper, F. *et al.* (2002) *Nature* **415**, 295-297. [2] Ceccarelli, C. *et al.* (2002) *Astron. Astrophys.* **395**, L29-L33. [3] Hofmeister, A.M. *et al.* (2004) *Geochim. Cosmochim. Acta* **68**, 4485-4503. [4] Tielens, A.G.G.M. *et al.* (1998) *Astrophys. Space Sci.* **255**, 415-426. [5] Gail, H.-P. *et al.* (1999) *Astron. Astrophys.* **347**, 594-616. [6] Toppani, A. *et al.* (2004) *Lunar Planet. Sci. Conf.* **XXXV**, #1726. [7] Anders, E., Grevesse, N. (1989) *Geochim. Cosmochim. Acta* **53**, 197-214. [8] Chen, L.-C. (1994) in *Pulsed Laser Deposition of Thin Films*, ed. Chrisey & Hubler, 167-198. [9] White, W.B. (1974) in *The infrared spectra of minerals*, ed. Farmer, 227-284. [10] White, W.B. (1971) *American Miner.* **56**, 46-53. [11] Payne, H.E. *et al.* (1988) *Astrophys. J.* **326**, 368-375. [12] Marret, S. *et al.* (2002) *Astron. Astrophys.* **395**, 573-585. [13] de Graauw, T. *et al.* (1996) *Astron. Astrophys.* **315**, L345-L348. [14] Boonman, A.M.S., van Dishoeck, E.F. (2003) *Astron. Astrophys.* **403**, 1003-1010.