



Gas–solid carbonation as a possible source of carbonates in cold planetary environments

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ARTICLE INFO

Article history:

Received 3 April 2012

Received in revised form

8 November 2012

Accepted 9 November 2012

Available online 1 December 2012

Keywords:

Carbonates

Gas–solid carbonation

Mars

Low temperature

Infrared microscopy

Ca and Mg hydroxides

ABSTRACT

Carbonates are abundant sedimentary minerals at the surface and sub-surface of the Earth and they have been proposed as tracers of liquid water in extraterrestrial environments. Their formation mechanism is since generally associated with aqueous alteration processes. Recently, carbonate minerals have been discovered on Mars' surface by different orbitals or rover missions. In particular, the phoenix mission has measured from 1% to 5% of calcium carbonate (calcite type) within the soil (Smith et al., 2009). These occurrences have been reported in area where the relative humidity is significantly high (Boynton et al., 2009). The small concentration of carbonates suggests an alternative process on mineral grain surfaces (as suggested by Shaheen et al., 2010) than carbonation in aqueous conditions. Such an observation could rather point toward a possible formation mechanism by dust–gas reaction under current Martian conditions. To understand the mechanism of carbonate formation under conditions relevant to current Martian atmosphere and surface, we designed an experimental setup consisting of an infrared microscope coupled to a cryogenic reaction cell (IR-CryoCell setup). Three different mineral precursors of carbonates (Ca and Mg hydroxides, and a hydrated Ca silicate formed from Ca_2SiO_4), low temperature (from -10 to $+30$ °C), and reduced CO_2 pressure (from 100 to 2000 mbar) were utilized to investigate the mechanism of gas–solid carbonation at mineral surfaces. These mineral materials are crucial precursors to form Ca and Mg carbonates in humid environments ($0\% < \text{relative humidity} < 100\%$) at dust– CO_2 or dust–water ice– CO_2 interfaces. Our results reveal a significant and fast carbonation process for Ca hydroxide and hydrated Ca silicate. Conversely, only a moderate carbonation is observed for the Mg hydroxide. These results suggest that gas–solid carbonation process or carbonate formation at the dust–water ice– CO_2 interfaces could be a currently active Mars' surface process. To the best of our knowledge, we report for the first time that calcium carbonate can be formed at a negative temperature (-10 °C) via gas–solid carbonation of Ca hydroxide. We note that the carbonation process at low temperature (< 0 °C) described in the present study could also have important implications on the dust–water ice– CO_2 interactions in cold terrestrial environments (e.g. Antarctic).

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1. Introduction

The biotic and abiotic (i.e. chemical) formation of carbonates plays a crucial role in the global carbon cycle on Earth. In addition, carbonate minerals often sequester various trace elements (actinides and lanthanides), metalloids, and heavy metals, and thus control in part their global cycling (e.g. Paquette and Reeder, 1995; Stumm and Morgan, 1995; Sigg et al., 2000). In general, carbonate minerals can be formed in natural or artificial environments by

three different mechanisms (e.g. Montes-Hernandez et al., 2010a): (1) aqueous nucleation-growth in homogeneous or heterogeneous systems (aqueous conditions), for example, the chemical or biogenic formation of carbonates in lakes, oceans, CO_2 storage sites, natural caves; (2) gas–solid carbonation of alkaline minerals (fine particles) in the presence of adsorbed water (water humidity conditions, $0 < \text{water activity} < 1$), for example carbonate formation in water–unsaturated soils, in terrestrial or extraterrestrial aerosols (Shaheen et al., 2010). This water has an important role in the surface chemistry of minerals as was shown by Galhotra et al. (2009) and Baltrusaitis and Grassian (2005) with zeolites and iron oxide surfaces; (3) dry gas–solid carbonation of granular/porous materials (dry conditions, water activity ≈ 0), for example, the industrial mineralization, recovery or capture of CO_2 at high

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temperatures in the presence of alkaline binary oxides (CaO, MgO) or metastable, nanoparticle alkaline silicates (Montes-Hernandez et al., 2012a, 2012b).

In the Planetary Sciences context, carbonates are generally considered as indicators of aqueous alteration processes (Bandfield et al., 2003; Milliken and Rivkin, 2009; Boynton et al., 2009; Ehlmann et al., 2008; Michalski and Niles, 2010). In the case of Mars, huge deposits of surface carbonates remained undetected for a long period, and their suspected absence was used to constrain the chemistry of a putative Martian ocean (Fairén et al., 2004). Evidences are now growing for the presence of carbonates at the surface of the red planet, which include observations of carbonate-rich outcrops (Ehlmann et al., 2008; Michalski and Niles, 2010) as well as carbonates within the Martian dust (Bandfield et al., 2003; Boynton et al., 2009). The aqueous alteration of mafic rocks in the presence of CO₂ is certainly an efficient mechanism for carbonate synthesis, an alternative pathway of carbonate synthesis exists, which does not require the presence of liquid water. This pathway involves reaction of a mineral substrate with CO₂ in the presence of chemisorbed water (few angstroms to few nm thick layers), and was recently tested and observed for terrestrial aerosols (Shaheen et al., 2010).

Here, we report on an experimental study of the kinetic of carbonation in liquid-water free environment. We designed novel, state of the art experimental setup (IR-CryoCell) to investigate the in situ gas–solid carbonation (i.e. resolved in time), for temperature and pressure conditions relevant to Mars. We studied carbonate synthesis starting from Ca and Mg hydroxides and an amorphous silicate (synthesized from Ca₂SiO₄), at low temperature (from –10 to +30 °C) and at low CO₂ pressure (from 100 to 2000 mbar). These starting materials are known precursors to form respective Ca and Mg carbonates in humid environments at dust–CO₂ or dust–water ice–CO₂ interfaces, at least under “terrestrial” conditions. They also can be expected to occur at the surface of Mars and some asteroids (Mg hydroxide has been described on Ceres). We report here laboratory experiments on gas–solid carbonation process at low temperature (< 0 °C), which provides new insights on conditions for carbonate formation. We will show that gas–solid carbonation can occur below the water frost point (at terrestrial atmospheric pressure), with significant implications on the dust/water–ice/CO₂ interactions in cold environments.

2. Materials and methods

The experiments were performed using three different materials, Ca, Mg hydroxide and a Ca silicate hydrate. CO₂ is known to react with surface of CaO and MgO by adsorption (Ochs et al., 1998a, 1998b) and produce carbonates as well the importance of OH groups to water adsorption on surfaces (Yamamoto et al., 2008). These substrates were chosen to mimic natural conditions and to catalyze reaction as their surfaces are terminated by OH groups: (i) in order to form Ca–Mg carbonate by reaction with CO₂, a Ca and Mg source is needed; (ii) the presence of hydroxyl groups in the starting material was requested to permit auto-catalysis of the reaction (Montes-Hernandez et al., 2010a); (iii) the material had to be geologically relevant.

Brucite has not been detected on the Martian surface. However, various types of phyllosilicates have been now described over the planet that are interpreted as aqueous alteration products of mafic rocks (see the recent review by Ehlmann et al., 2011). Such aqueous alteration processes can be accompanied by the production of brucite (Evans, 2008). Identification of brucite by its spectral properties is difficult since no diagnostic band is present in the NIR, with the exception of the 2.7 μm feature

ubiquitous to almost all –OH bearing phases. Brucite has been diagnosed on some asteroids from observations in the mid-IR (together with carbonate). It is the case of the largest main-belt object, Ceres. In addition, MgO has been proposed as a condensation product in some solar nebula models, which should readily transform to brucite in the presence of gaseous water or humidity (Gail and Sedlmayr, 1999).

Portlandite has not been reported on Mars either. On Earth, it is almost always found in association with calcium carbonates, and is very difficult to observe due to its high reactivity with CO₂. We chose to study portlandite because of its high catalytic reactivity which enabled to provide kinetic measurements under some hours. In addition, it is a structural analog to brucite and a number of X-(OH)₂ type hydroxide compounds (where X = Ni, Co, Fe, Mn, Cd). CaO has also been proposed as an intermediate compound by Shaheen et al. (2010) to explain the formation of calcium carbonate on Mars, which could readily transform to portlandite in the presence of gaseous H₂O or humidity.

Finally, we used an amorphous calcium silicate hydrate synthesized from larnite (Ca₂SiO₄). This material was chosen to represent an amorphous volcanic material. Volcanic activity has been widespread on Mars, and volcanoclastic deposits have been described (Ehlmann et al., 2011). We decided to use a pure calcium amorphous silicate (rather than a basaltic glass), in order to simplify the chemistry of the system. However, one might expect a more complex chemistry for Martian volcanic glasses. Our approach might appear too simplistic, but might provide grounds for understanding more complex chemistries.

2.1. Materials

2.1.1. Portlandite

Calcium hydroxide Ca(OH)₂ was provided by Sigma-Aldrich with 96% chemical purity (about 3% of CaCO₃) and 1% of other impurities. This material is characterized by platy nanoparticles (sheet forms) forming micrometric aggregates with high porosity and/or high specific surface area (15 m²/g). Its infrared spectrum has revealed a small amount of adsorbed water at atmospheric conditions, around 0.01g H₂O/g Ca(OH)₂ determined by TGA. The portlandite sample was used without any physicochemical treatment.

2.1.2. Brucite

Magnesium hydroxide Mg(OH)₂ was provided by Fisher Scientific (UK). This material is characterized by platy hexagonal microparticles. A small amount of adsorbed water at atmospheric conditions was detected by infrared spectroscopy. The brucite sample was crushed in a mortar before use.

2.1.3. Amorphous calcium silicate hydrate

This material was synthesized from synthetic larnite mineral (Ca₂SiO₄) by using a simple acidic treatment (2 M HCl solution) at room lab temperature during 15 minutes. Then, consecutive dilutions with demineralized water were carried out until pH equal to 3. Finally, the solid was separated from the solution by centrifugation (10 min at 12 000 rpm) and dried directly in the centrifugation flasks at 80 °C for 48 h. The larnite synthetic mineral was provided by Santos and it was synthesized as reported in Santos et al. (2009).

2.1.4. Carbon dioxide

Carbon dioxide CO₂ was provided by Linde Gas S.A. with 99.995% of chemical purity. This gas was directly injected in the cryogenic reaction cell without any treatment or purification.

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