Inorganic carbon transformations between phases and its impact on its isotopic signature under open conditions

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ABSTRACT

In order to evaluate the possibility of tracing dissolved inorganic carbon (DIC) derived from calcite dissolution under open system conditions, controlled laboratory experimen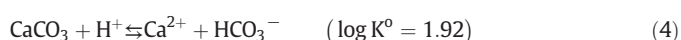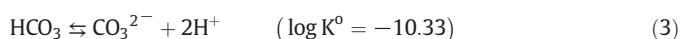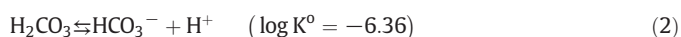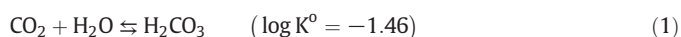ts using stable carbon isotopes were conducted in a specially designed reaction chamber with constant pH monitoring. The system design also allowed us to measure the forward and backward (degassing) gas transfer reactions rates. We confirmed that the degassing reaction rate can be two to four times slower than the gas transfer reaction rate depending on the differences in pCO_2 between the gas phase and the liquid. The isotopic analyses suggest that the carbon isotopic signature of DIC under open system conditions is controlled by the CO_2 carbon isotopic signature, the isotopic fractionation between CO_2, the relative occurrence of the different DIC species, and changes in pH. We found that the isotopic signature of DIC is not affected by the isotopic signature of the calcite or the mechanism controlling the dissolution (protonation or hydration). Practically this study suggests that it is not possible to trace the DIC derived from calcite dissolution under open system conditions. It supports the approach of evaluating the pedogenic carbonate content by stable carbon isotopes methods. In open system conditions: a) pH can explain up to 8‰ variation in the DIC $\delta^{13}C$ signature and b) temperature is the second most important factor affecting the δC^{13}-DIC signature, and only at pH above neutrality.

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1. Introduction

In general, shallow soil zones and the surface of water bodies are considered to be open systems with respect to CO_2 reactions (Nordt et al., 1996; Jin et al., 2009; Khadka et al., 2014). It may be considered as a pure closed system when soils are saturated and in deeper layers of water, in which there is no contribution of atmospheric CO_2. In arid and semiarid soils, it is more likely that soils act as an open system and therefore we focused on this condition.

The following reactions are involved in dissolution of calcite by carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (\log K^o = -1.46) \qquad (1)$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad (\log K^o = -6.36) \qquad (2)$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + 2H^+ \qquad (\log K^o = -10.33) \qquad (3)$$

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \qquad (\log K^o = 1.92) \qquad (4)$$

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (\log K^o = -5.9) \qquad (5)$$
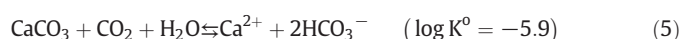
Eq. 5 suggests that for every mole of calcite that is dissolved, one mole of CO_2 is consumed, and in the reverse form, for every mole of calcite that is precipitated, one mole of CO_2 is released.

In soils, the rate of change of solid carbonate content is relatively slow. Sites with a reliable long-term record related to soil inorganic carbon (SIC) are very limited. Eshel et al. (2007) demonstrated the complexity involved in studying changes in the SIC content (as calcite) in soils. Because calcite dissolution by carbonic acid is considered carbon sequestration (Suarez, 2000; Nordt et al., 2000; Drees et al., 2001, Monger et al., 2015), understanding changes in the dissolved inorganic carbon (DIC) budget are essential to understanding SIC sequestration.

Attempts to predict carbonate precipitation or dissolution in irrigated soils based on the level of saturation of the soil solution with respect to calcite have proven to be ineffective (Levy, 1984). This researcher found that even when the water used for irrigation was undersaturated with respect to calcite, carbonate accumulation occurred. Levy (1984) related this behavior to the effect of the cation exchange complex of the soil, to dissolution of minerals other than calcite and to the fact that calcite is not the only solid form of carbonate in the soil. Suarez and Rhoades (1982) concluded that soils and drainage water are rarely at equilibrium with calcite and that the use of calcite solubility

is inappropriate for models predicting carbonate dissolution–precipitation in arid or semi-arid regions. They also suggested that kinetics rather than equilibrium relations control soil solution composition. Thus, the slowest reaction, will control the overall reaction of carbonate precipitation or dissolution (Morse and Arvidson, 2002; Hansen et al., 2013). Inskeep and Bloom (1985) found that the main mechanism of calcite dissolution and precipitation at low CO_2 partial pressure (pCO_2) < 0.01 atm and high pH (>8) can be visualized as Ca^{2+} and CO_3^{2-} forming $CaCO_3$ at the surface of the already present mineral. These results are in agreement with those of Plummer et al. (1978) and Nancollas and Reddy (1971). Arvidson and Mackenzie (2000) found good agreement between the difference in the energy needed for the hydration of calcium and magnesium and between the tendency of the carbonate to precipitate as the Ca or Mg salt. It was suggested that the hydration of CO_2 and pCO_2 is limiting for calcite dissolution in a H_2O, CO_2 and $CaCO_3$ system (Amrhein et al., 1985; Dreybrodt et al., 1996). Hansen et al. (2013) experimentally separated calcite precipitation into a three step process by studying degassing from a 0.1 mm film. The three steps were CO_2 degassing, re-equilibrium and precipitation, with each subsequent step one order of magnitude slower than the previous one. The system becomes more complex when organic carbon is involved. It was found that the rates of dissolution and precipitation of calcite are greatly inhibited in the presence of organic matter (Amrhein and Suarez, 1987; Inskeep and Bloom, 1986; Lebron and Suarez, 1996). The presence of Mg, Na and Si species also affects the precipitation rate and the apparent solubility of calcium carbonate when the solution is over-saturated with respect to calcite (Levy et al., 1995; Miyamoto and Pingitore, 1992). An enhanced effect of biomineralization on the dynamics of soil carbonate formation has been noted in the literature as well (Phillips et al., 1987; Monger et al., 1991; Stocks-Fischer et al., 1999; Warren et al., 2001).

In order to overcome the need for the complex data required for good prediction of inorganic carbon turnover based on geochemistry models, we studied the feasibility of using carbon isotopes to trace the DIC derived from calcite dissolution under open system conditions.

2. Materials and methods

2.1. Reaction chamber design

A 17 cm long 10 cm inside diameter Plexiglas column, capped on both sides, was used as a vertical reaction chamber (Fig 1). The chamber was filled with 750 mL distilled water while the upper half was exposed to a constant gas flow of 40 cm^3 min^{-1}. An inlet and outlet for gas was placed on opposite sides of the chamber at the midpoint of the headspace. Each was fitted with a one-way valve that restricted gas flow to one direction. In addition a combined pH electrode (Cole-Palmer, U.S.A., model P-05001-70) and a solution sampling point (a septum) were installed at the midpoint of the liquid phase (Fig. 1). Approximately 1 g of calcite was placed in a small plastic cup, which was attached to a magnet. The cup and the magnet were fixed inside the chamber to the upper part of the chamber wall with a second magnet attached to the outside of the chamber. This allowed the calcite to be added to the water without opening the chamber by flipping the outside magnet (Fig 1).
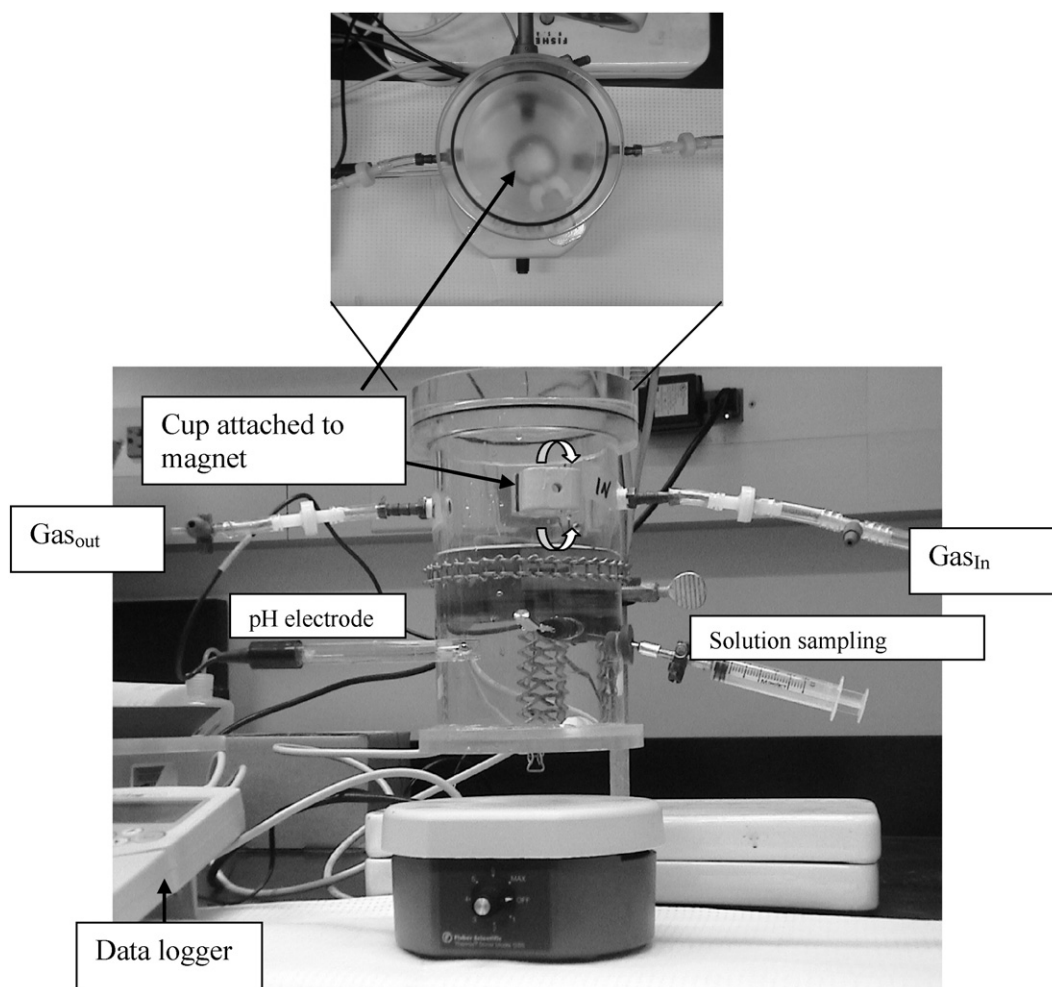

Fig. 1. Reaction chamber design.