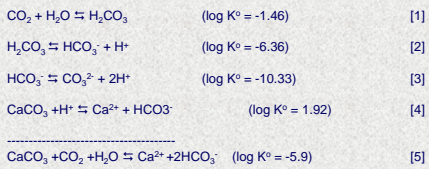


Introduction

- ❖ The potential for soil inorganic carbon (SIC) sequestration and its mechanisms are still in question.
- ❖ Sites with a reliable long-term record related to SIC are very limited.
- ❖ The rate of change in carbonate content in soils is relatively slow compared to that of soil organic carbon (SOC).
- ❖ Disagreement appears in the literature whether precipitation of carbonate solid should be considered as sequestration or whether dissolution of solid carbonate should be considered as sequestration.

Background

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



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.

The chemistry and the carbon budget of DIC are directly affected by the degree of system opening to the atmosphere (the existence of infinite gas phase), $p\text{CO}_2$, and pH.

Objective

- ❖ To study the feasibility of using carbon isotopes to trace the DIC derived from calcite dissolution under open system conditions

Approach

- ❖ Controlled dissolution experiments under open system conditions and stable carbon isotopes.

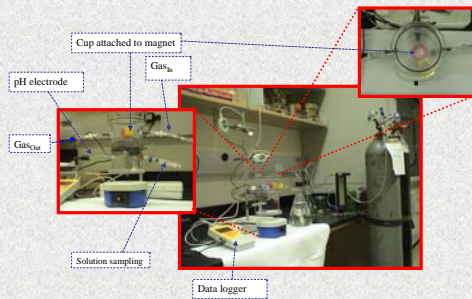


Figure 1: The experimental system

Calcite and CO_2

Two sources of calcite were used: 1) analytic calcite (Fisher) with $\delta^{13}\text{C} = -18.2 \pm 0.1\%$, and 2) marble (Calacatta Supreme, Alpha Granite&Marble), which has a $\delta^{13}\text{C}$ signature of $2.1 \pm 0.4\%$.

Four different $p\text{CO}_2$ were used: 0.9998, 0.03, 0.0003 and 0.00003 (all balanced with N_2). The CO_2 had a signature of $\delta^{13}\text{C} = -35.3 \pm 0.1\%$.

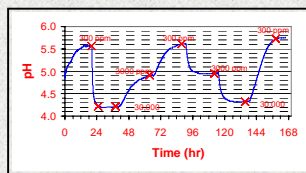


Figure 2: The pH response to the $p\text{CO}_2$ changes in a $\text{H}_2\text{O}/\text{CO}_2$ system as measured in the reaction chamber

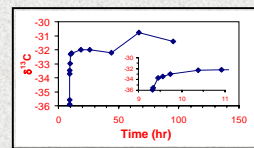


Figure 4: The changes in DIC $\delta^{13}\text{C}$ signature as a function of time after addition of calcite with $\delta^{13}\text{C}$ calcite = $2.1 \pm 0.1\%$ addition.

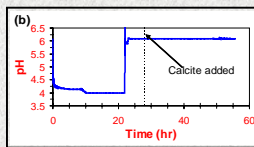
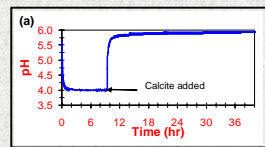


Figure 3: An example of the measured pH as a function of time in a controlled calcite dissolution experiment (a) with no addition of external base (b) with the prior addition of NaOH.

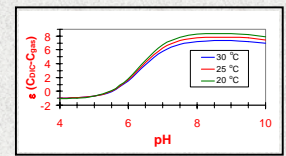


Figure 5: The estimated isotopic fractionation (ϵ) between DIC and $\text{CO}_2(\text{g})$ as a function of pH at three different temperatures. The calculation is based on carbonate species fractionation at varying temperature adopted from Vogel et al., (1970) for $\text{CO}_2(\text{aq})$ - $\text{CO}_2(\text{g})$; Mook et al., (1974) for HCO_3^- - $\text{CO}_2(\text{g})$; and Deines et al., (1974) for CO_3 - $\text{CO}_2(\text{g})$.

	No calcite	$\delta^{13}\text{C}_{\text{calcite}} = -18.2\pm$	$\delta^{13}\text{C}_{\text{calcite}} = 2.1\pm 0.4\%$
Calcite used to raise the pH	$35.6 \pm 0.5\%$	$31.8 \pm 0.3\%$	$31.6 \pm 0.5\%$
Calcite added after the pH was adjusted to 6.01 with NaOH	$35.4 \pm 0.5\%$		$31.4 \pm 0.6\%$

Table 1: A summary of $\delta^{13}\text{C}_{\text{DIC}}$ values under equilibrium with gas $p\text{CO}_2$ 1 atm which has a signature of $\delta^{13}\text{C}_{\text{CO}_2} = -35.3 \pm 0.5\%$ as measured in different treatments

CONCLUSIONS

- ❖ The long-term continuous pH measurement was a powerful indicator of the system conditions. The pH electrode drift was found to be not more than 0.2 pH units after 7 days in DI water (Figs. 2 and 3)
- ❖ The isotopic signature of DIC is not affected by the isotopic signature of the calcite or the mechanism controlling the dissolution (carbonic acid or hydration) (Table 1).
- ❖ The DIC isotopic signature under open system conditions is highly affected by isotopic fractionation between DIC and CO_2 .
- ❖ The results confirm the model suggested by Deines et al., (1974) and Clark and Fritz, (1997) who suggested that under open system conditions the solid carbonate does not affect the DIC isotopic signature.
- ❖ It is not possible to trace the DIC derived from the calcite dissolution under open system conditions by stable isotope techniques because of the gas/water isotopic fractionation that obscures the contribution of the different C sources.