



Adsorption isotope effects for carbon dioxide from illite- and quartz-packed column experiments

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ABSTRACT

The transport of gas through porous media can be affected by diffusion and advection, reaction with solid and liquid phases, and adsorption onto solid substrates. Stable isotope substitution within a gas affects its adsorption affinity, solubility and diffusion coefficients and therefore isotope fractionation occurs with these processes. Adsorption of CO₂ onto dry solid substrates has been shown to have an apparent inverse isotope effect whereby ¹²CO₂ is preferentially retained during chromatography compared to ¹³CO₂. Here, carbon isotope compositions are reported for CO₂ eluted from 1-dimensional flow-through column experiments on dry geologic substrate including quartz sand and crushed illite. An analytical solution to a coupled advection–diffusion–adsorption equation is developed to fit the carbon isotope data and interpret the results from each experiment and a Rayleigh fractionation model is used to interpret adsorption results. Adsorption results from the illite-packed column are shown to closely follow a Rayleigh fractionation model with an alpha value ($\alpha_{\text{adsorbed-gas}}$) of 0.9909 whereas only diffusion and advection are required to describe the empty and quartz-packed columns with a diffusivity (D) ratio of 0.9991 between ¹³CO₂ and ¹²CO₂. These results demonstrate that adsorption isotope effects may significantly change the $\delta^{13}\text{C}$ value of CO₂ that is transported across dry geologic media and these effects should be considered in carbon capture and storage (CCS) leakage detection studies and studies attempting to accurately source CO₂ respired in soils under transient state conditions. Isotope effects associated with CO₂ adsorption in partially or fully water-saturated geologic media should be investigated in the future.

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1. Introduction

Transport of gas through porous media is a process fundamental to a wide range of geological studies. Stable isotope measurements have been used to delineate pathways of natural gas migration from source rock to reservoirs (Coleman et al., 1977; Wu et al., 1998), monitor the transport of CO₂ injected during sequestration projects (Benson and Cole, 2008), and understand gas transfer through the vadose zone and soil horizons (Cerling, 1984; Stern et al., 1999; Scanlon et al., 2002). Stable isotope compositions of subsurface gases such as CO₂ and methane can be used to distinguish and identify potential sources of subsurface gases. It is therefore important to understand isotope effects that may occur during transport of gases through various geological substrates. Considerably more research has been published on adsorption stable isotope effects related to mass transfer of methane and natural gas through water saturated geological media than published for CO₂ (e.g., Galimov, 1967; Fuex, 1980; Zhang and Krooss, 2001; Bacsik et al., 2002; Xia and Tang, 2012). Other studies have documented hydrogen and some limited carbon isotope effects for methane using laboratory-based temperature controlled gas chromatographic column experiments (e.g., Gant and Yang, 1964; Bruner et al., 1966; di Corcia and

Liberti, 1969; Fuex, 1980). The column materials in these experiments include glass, etched glass, squalane-coated glass, and charcoal. These experiments were conducted between temperature ranges of 0 and 190 °C to further develop and apply the statistical theory of isotope effects to condensed systems (Bigeleisen et al., 1963; Van Hook, 1967). Fuex (1980) argues that although carbon and hydrogen isotope adsorption effects may occur for methane under dry conditions, adsorption effects will not be significant in natural water-saturated systems. A thorough literature review found only two studies that documented chromatographic carbon isotope effects for CO₂ (Gunter and Gleason, 1971; Meier-Augenstein, 2004). Gunter and Gleason (1971) measured carbon and oxygen isotope fractionation of CO₂ as a result of adsorption on silica gel and Porapak Q gas chromatograph columns. The study of Gunter and Gleason (1971) demonstrates that under dry conditions, ¹²CO₂ is preferentially retained by the chromatographic material at elevated temperatures of 100 °C. Up to 30% differences in $\delta^{13}\text{C}$ were measured between injected CO₂ and CO₂ collected at different points along the chromatographic peak. Although studies have looked at CO₂ transport through porous media in shallow soil horizons and deeper geological conditions, the potential of adsorption isotope effects is not discussed. For example, Cerling (1984) developed an analytical model for CO₂ production and diffusion in soils. Stern et al. (1999) demonstrated that the oxygen isotope composition of soil CO₂ is predominantly affected by soil water and soil temperature, and to a lesser extent by the

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rate of exchange between oxygen in soil CO_2 and water, soil respiration rates, diffusivity, porosity, and advection.

This study documents carbon isotope compositions of CO_2 eluted through packed 1-dimensional flow-through columns to better understand adsorption isotope effects related to the transport of CO_2 through geologic substrates. An empty column is used to identify diffusion dominated isotope effects whereas quartz-packed and illite-packed columns are used to identify dispersion and adsorption related isotope effects, respectively. Illite was chosen because it is a common clay mineral in sediments and sedimentary rocks. Other common clay minerals, such as smectites, and organic compounds should be studied in the future to evaluate whether or not the magnitude of isotope fractionation factors varies with the substrate. Experimental results are modeled with an analytical 1-dimensional mass transport equation that incorporates advection, diffusion and adsorption (retardation). The illite experimental data are also modeled with the Rayleigh equation to determine a fractionation factor for the adsorption of CO_2 onto illite under dry conditions, which would represent a possible end member for the maximum adsorption isotope effect. Understanding potential differences in isotope effects between diffusion-dominated and adsorption-dominated systems may play an important role in understanding the transport of gases in the subsurface. This understanding may be used to attribute fugitive gases to potential sources or to simulate transient state soil CO_2 profiles. In addition to source attribution and flux studies, the measurement of stable isotope profiles of gas plume fronts may be used to interpret transport histories of migrating gases through low transmissivity geologic layers such as cap rocks in CO_2 sequestration plots.

2. Methods

Experiments in this study were optimized to ensure that a large number of samples could be collected along the CO_2 chromatographic front eluting from a 1-dimensional flow-through column. A constant concentration step-function tracer injection was chosen to simplify the experiment, to ensure that a large number of data points could be sampled, and to focus on possible changes in adsorption phenomena as the substrate reached saturation. The concentration of the injected

gas (5000 ppmv in a balance of helium) was chosen to work within the optimal range of the isotope ratio mass spectrometer. Through trial and error the lengths and diameter of the experimental columns and flow rates were chosen to provide sufficient experimental data points (50–100) in a reasonable amount of time (<24 h).

2.1. Experimental platform and isotope measurements

The experimental platform used in this study is illustrated in Fig. 1. It consists of 4.57 mm diameter polished stainless steel tubing placed inline and directly downstream of a mass flow controller (Alicat Scientific MC-55SCC-D) that is downstream of a gas switching valve (Swagelok SS-43Z6FS1). The column was wrapped in foam insulation and a thermometer was attached to the column to monitor temperature throughout the experiment. Fittings and tube connections are either 1/16" stainless steel or fused silica capillary. This relatively simple system is necessary to minimize dead volume and maintain constant flow rates. Depending on the column packing, the total pore volume of the system was between 16 and 24 ml whereas the total dead volume was 2.3 ml. Downstream of the column is an automated gas sampling valve in a Thermo Fisher Scientific GasBench II (Bremen, Germany) fitted with a fixed volume 100 μl sample loop. Sampled gas is directed through a Poraplot Q gas chromatograph column (25 m, 0.32 mm, Varian) and a Nafion® (Permapur, Toms River, New Jersey) gas drier. Chromatographic separation of CO_2 required approximately 2.5 min, defining the minimum sampling time interval.

To remove as much water as possible and desorb CO_2 from mineral surfaces prior to an experiment, the experimental column was conditioned for 3 days at 60 °C by purging at 5 ml/min with dry helium gas. The effluent gas was monitored for nitrogen and carbon dioxide during the conditioning period, the concentrations of which were observed to fall below detection limits, similar to an analytical blank when no experimental column is attached. Following the conditioning period the flow rates were stabilized to 0.5 ml/min and background CO_2 concentrations were measured for one full day. After the background CO_2 concentrations were sufficiently stabilized, the gas selector valve was switched from pure helium to the 5000 ppmv mixture of CO_2 and helium. The

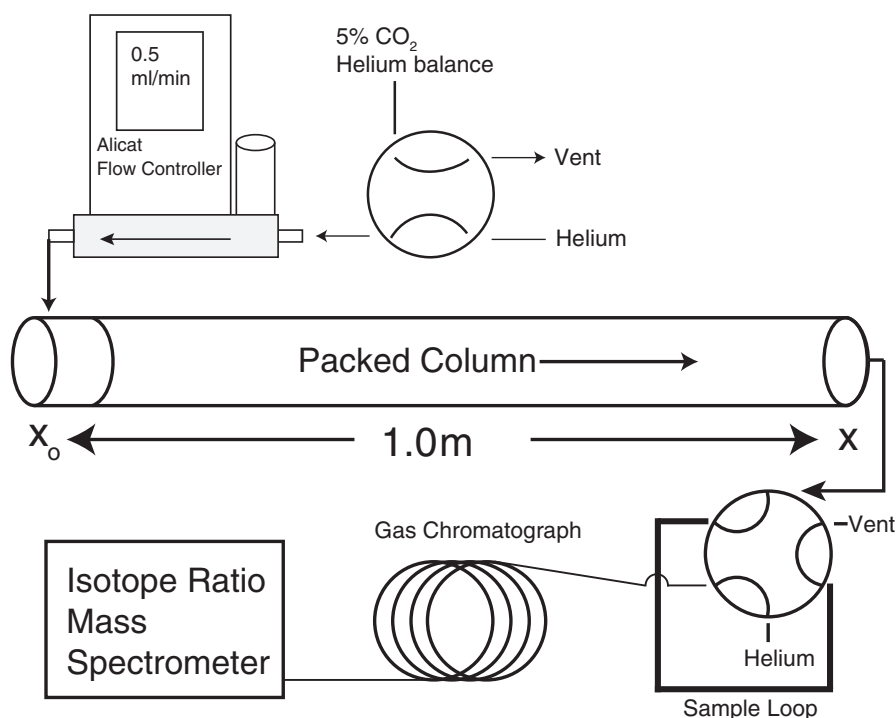


Fig. 1. Experimental set up.

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