Note: A dual temperature closed loop batch reactor for determining the partitioning of trace gases within CO2-water systems

Oliver Warr, Christopher A. Rochelle, Andrew J. Masters, and Christopher J. Ballentine

---

Articles you may be interested in

Tunable diode laser absorption spectroscopy-based tomography system for on-line monitoring of two-dimensional distributions of temperature and H2O mole fraction
Rev. Sci. Instrum. **87**, 013101 (2016); 10.1063/1.4939052

Gas temperature measurements inside a hot wall chemical vapor synthesis reactor
Rev. Sci. Instrum. **83**, 114904 (2012); 10.1063/1.4766956

A calorimetric method to determine water activity
Rev. Sci. Instrum. **82**, 114903 (2011); 10.1063/1.3660815

A dynamic gravimetric standard for trace water
Rev. Sci. Instrum. **82**, 105102 (2011); 10.1063/1.3642660

Spatially resolved electron temperatures, species concentrations, and electron energy distributions in inductively coupled chlorine plasmas, measured by trace-rare gases optical emission spectroscopy
J. Appl. Phys. **91**, 6288 (2002); 10.1063/1.1467398
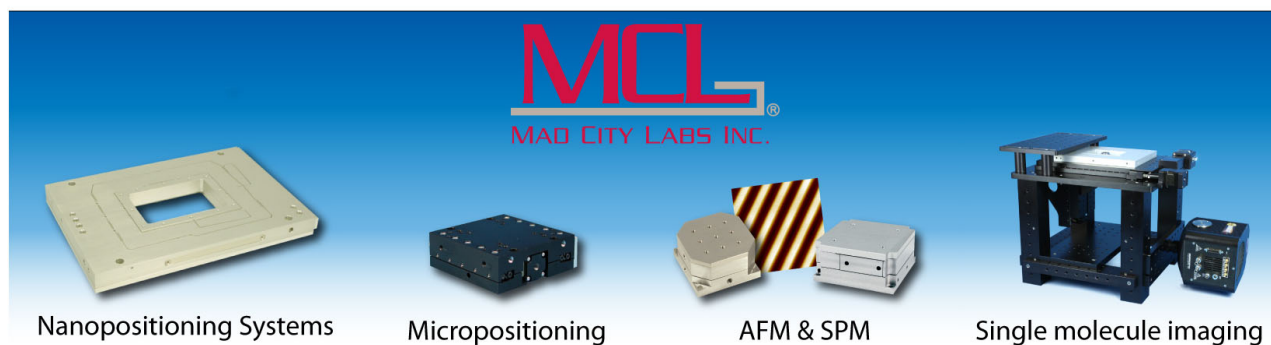
Note: A dual temperature closed loop batch reactor for determining the partitioning of trace gases within CO₂-water systems

Oliver Warr,[1,a),b)] Christopher A. Rochelle,[2] Andrew J. Masters,[3] and Christopher J. Ballentine[1,a)]

[1]*Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, United Kingdom*
[2]*British Geological Survey, Environmental Science Centre, Nicker Hill, Keyworth, Nottingham NG12 5GG, United Kingdom*
[3]*School of Chemical Engineering and Analytical Science, University of Manchester, Manchester M13 9PL, United Kingdom*

An experimental approach is presented which can be used to determine partitioning of trace gases within CO_2-water systems. The key advantages of this system are (1) The system can be isolated with no external exchange, making it ideal for experiments with conservative tracers. (2) Both phases can be sampled concurrently to give an accurate composition at each phase at any given time. (3) Use of a lower temperature flow loop outside of the reactor removes contamination and facilitates sampling. (4) Rapid equilibration at given pressure/temperature conditions is significantly aided by stirring and circulating the water phase using a magnetic stirrer and high-pressure liquid chromatography pump, respectively. © *2016 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4938159]

Experimentally deriving accurate partition coefficients of inert tracers (such as noble gases) for binary phase systems are extremely important for indirectly interpreting key geological systems. These data can be used to determine locations of hydrocarbon reservoirs,[1,2] understanding natural analogues for Carbon Capture and Storage (CCS) projects,[3,4] constraining water recharge temperatures and rates in natural aquifers,[5,6] and indicating hydrothermal fluid origin and evolution within gold mineralisation zones.[7,8] The simplest way to experimentally derive partitioning for these tracers requires injecting a tracer-rich spike into closed system of interest, then collecting representative samples from both phases while the system is fully at equilibrium under specified P,T conditions. This requires a specially constructed experimental system. It needs to be able to completely contain a pressurized system at the specified temperature and pressure, rapidly reach equilibrium and allow concurrent sampling of both phases. However, there are 2 inherent problems with such experiments:

(1) Sampling can cause depressurization and degassing.
(2) Even minute gas bubbles adhering to the walls of the water samplers can greatly alter partitioning data.

Both issues have the potential to invalidate the experimental results. This is especially true in the case of noble gases which are highly susceptible to disequilibrium and air contamination. A novel approach is presented here, which minimizes these problems. As verification we have applied it to generate noble gas partitioning data. The resulting high-pressure experimental layout for sample generation is depicted in Figure 1.

The system used a 550 bar rated 200 cm³ stainless steel reactor. The head of the reactor was welded in place in order to prevent leakage. The reactor head had three 1/8 in. tapered Swagelok connections; one to allow CO_2 to be added and subsequently pumped for CO_2 phase sampling, and the other two to allow water to be cycled out of the reactor via the water samplers. The only moving parts were a polytetrafluoroethylene (PTFE)-coated magnetic stirrer bead inside the vessel (to ensure equilibration between water and gas phases) and a pair of sapphire pistons in the high-pressure liquid chromatography (HPLC) pump (to circulate water out of the reactor and through the samplers).

Inserted into the reactor was a 1/8 in. titanium "dip tube" close to its base for the extraction of the aqueous phase. The other two connections into the reactor were for aqueous phase return and CO_2 injection/sampling. These were both 1/8 in. 316 stainless steel tubes that terminated in the CO_2-filled headspace of the reactor. The valve on the CO_2 line was a double valve to facilitate both sampling and addition of extra CO_2 to enable a range of pressure conditions to be investigated. All three of these lines were connected to Top Industrie stainless steel valves rated to 1000 bar. Flow lines outside of the reactor comprised mainly 1/8 in. 316 stainless steel tubing with SS-ORS2 Swagelok needle valves. Two short lengths of 1/16 in. tubing were used to connect to the HPLC pump.

Charging the reactor first involved addition of approximately 100 ml of deionized water. The headspace of the reactor (100 cm³) was then flushed with pure, laboratory-grade CO_2 continuously at 1 bar pressure for 5 min to displace and minimize the air component within the headspace. Next, all connections were securely tightened and the reactor pressurized to approximately 30 bar using an ISCO 500HP syringe pump, and the integrity of connections tested using an
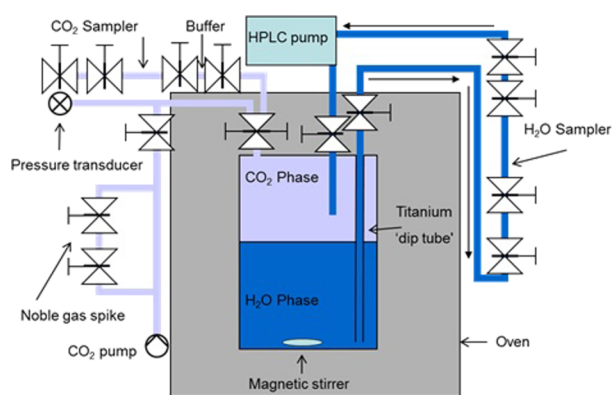

FIG. 1. A schematic diagram of experimental layout. The water phase was stirred within the reactor and circulated through the samplers via a HPLC pump. All valves, unless specified in the text, are SS-ORS2 Swagelok needle valves. Details of samplers and the valves used are shown in Figure 2. The figure has been modified from Warr *et al.*[9]

approved detergent-based leak detector. The reactor pressure was then monitored by a pressure transducer and logged over several days to verify that the reactor was leak-tight.

After this, the water circulation line was tested. This involved bleeding air out of the line in 3 steps. First, the water samplers (Figure 2) were loosely connected together and then connected to a JASCO PU-2086 HPLC pump. An ISCO 500HP pump was temporarily attached and used to slowly push the deionized water through these at a rate of 1 cm^3/min to displace any air. After a minute of bleeding water through these connections, they were fully tightened and this section of the line was isolated with valves. The sections of the circulation line exiting/entering the reactor were similarly purged of air by slowly allowing the CO_2 pressure within the reactor from before ($\sim$30 bar) to drive either water or CO_2 through these loosely connected sections of the line which were connected to either the base of the samplers or the HPLC pump. After a minute of bleeding water/CO_2, these connections were also fully tightened. All valves on the water line were then fully opened, the HPLC pump was switched on at a rate of 0.1 cm^3/min, and the water was allowed to circulate in a loop, as depicted in Figure 1. The constant HPLC flow rate ensured the contents of a water sampler were fully replaced every 15 min with freshly equilibrated water and the entire water phase was cycled through the sampling apparatus every 17 h. The system was also stirred using a magnetic stirrer bead (set to rotate at 300 rpm). Prior to each experiment, the system was partly pressurized up to 30-40 bar, the oven set to the required temperature, and the system left for 24 h to thermally equilibrate.

A 1.5 cm^3 noble gas spike containing 32% helium, 32% neon, 17% argon, 11% krypton, and 8% xenon at 0.5–0.8 bar
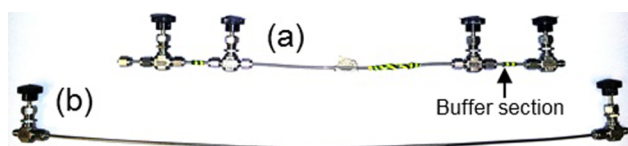

FIG. 2. Samplers used to collect samples from the CO_2 (a) and water phase (b). The CO_2 samplers included a buffer section to ensure sample integrity. Sampler volumes were $\sim$1 cm^3 and $\sim$1.5 cm^3, respectively.

was connected to the CO_2 pump as shown in Figure 1. This was flushed through with laboratory-grade CO_2 creating a noble gas-enriched CO_2 charge that was injected into the reactor. The system was then pressurized to 80%–90% of the desired experimental pressure and left to equilibrate with the system. During this equilibration process, the total pressure fluctuated due to both thermal expansion of the CO_2 and CO_2 dissolution into the water. Monitoring the pressure of the CO_2 phase via the pressure transducer therefore served as a reasonable proxy for phase equilibrium. System stability was typically reached within 24 h and always within 48 h of spike injection. Once system pressure had stabilized, it was adjusted to run conditions by either adding or removing minor amounts of CO_2. The system was then left isolated for at least 7 days to reestablish equilibrium during which the water phase was both stirred and circulated as before. The system was then considered to be fully equilibrated, as, even without the added benefit of stirring/circulating, diffusive processes alone would result in full thermodynamic equilibrium.[1] One hour prior to sampling, equilibrium was also verified by monitoring the system pressure.

The key aspects of the experimental arrangement are as follows:

(a) Circulation of the water ensures representative water composition in the samplers, provided that experiments are run for several days to ensure equilibration.

(b) The samplers are at a lower temperature relative to that of the reactor (in an oven). As the solubility of gases in this study increases with decreasing temperature, then any microscopic bubbles trapped in the samplers will be dissolved and excess ("contaminant") gas removed.

(c) The pump is placed after the samplers, minimizing any disturbance to the fluid being sampled.

(d) Water phase sampling involves isolating the samplers and removing them from the flow loop—there is no pressure drop or other "disturbance" during sampling, and hence minimal opportunity for gas exsolution.

All water and CO_2 samples were collected in 0.2159 cm (0.085 in.) internal diameter stainless steel tubes with all-metal stainless steel Swagelok SS-ORS2 needle valves at each end able to maintain pressure to 230 bar. All connections used standard 1/8 in. tube fittings. As an additional precaution, the CO_2 samplers included a small buffer section at each end to ensure sample integrity.

Samples of CO_2 and water for each data point were collected in triplicate, with samplers connected in series. The methodology for sampling each phase was as follows: at least 30 min prior to sampling, the magnetic stirrer was turned off to allow any entrained gas bubbles to separate from the water. At the same time a high precision platinum temperature probe with an accuracy of ±0.2 K was inserted into the oven and left to thermally equilibrate. Once the 30 min had elapsed, the experimental pressure and temperature were recorded from the pressure transducer and temperature probe, respectively. For sampling, the HPLC pump was turned off and the valves to the water samplers were closed sequentially starting from the closest to the HPLC pump. Once all water sampler valves were closed (i.e., water samples have been
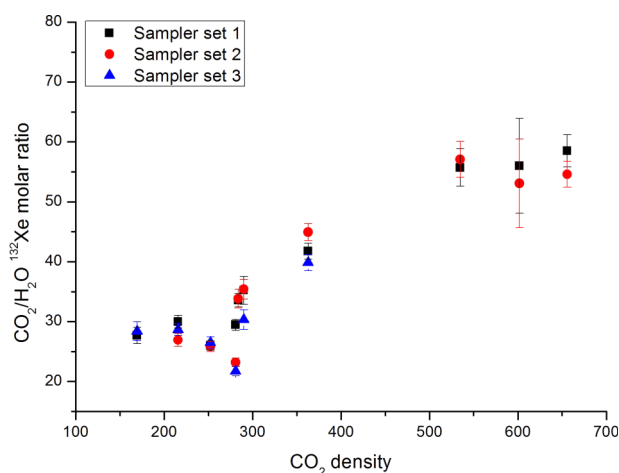
FIG. 3. Molar ratios for ^{132}Xe as a function of CO_2 density for different sampler sets. Data have been excluded, where post-sampling contamination was identified (i.e., during storage transport or analysis). 1 σ error bars are principally derived from analytical and P,T measurement uncertainty.

collected), the isolation valves for the water samplers were closed. The pressure transducer was also isolated at this time. The CO_2 samplers were connected in series and attached to the reactor at the CO_2 inlet/outlet valve within the oven. Valves were subsequently fully opened in sequence so as to allow CO_2 from the reactor to pressurize the samplers one at a time. When all samplers were fully pressurized, the last valve in the series was slightly opened to vent any air-contaminated CO_2. Typically 120-130 cm^3 (at STP) of CO_2 was flushed through the samplers to purge them off any air, the valves closed in reverse sequence, and the samplers removed. The water samplers were also removed at this stage. Isolating the water samples first prevented potential degassing as a consequence of slight depressurization during gas sampling.

Subsequent experiments involved replacing the water samplers in the flow line (Figure 1), removal of any air as described above, and re-equilibration at a new set of pressure-temperature conditions. The relatively large volume of water in the reactor meant that several experiments could be taken before this needed topping up. Typically 3 experiments could be performed before an additional noble gas spike was required. The parts of the system most susceptible to wear and tear were the two seals around the pistons in the HPLC pump. Potential leaks were prevented by replacing these seals every 3 months.

Samples collected were analyzed for their noble gas content using a Hiden Analytical 1–200 amu (HAL200) quadrupole mass spectrometer at the University of Manchester. A detailed description of this process is provided in the work of Warr et al.[9] From the analysis, three unitless CO_2-H$_2$O noble

gas molar ratios were obtained for each isotope as a function of CO_2 density. The data from ^{132}Xe are presented in Figure 3.

The reproducibility from multiple samples highlighted in Figure 3 indicated that the sample generation technique presented here can be used to generate valid, reproducible data for publication.[9]

To summarize, the key advantages of the experimental system outlined here are as follows:

(1) This set up is fully self-contained. This makes it ideal for conducting multiphase experiments involving conservative tracers such as noble gases.
(2) The ability to sample both phases concurrently allows for accurate determination of tracers within each phase for specified P,T conditions.
(3) The same system can be easily adapted to sample new P,T conditions.
(4) Use of an HPLC pump and a magnetic stirrer allows for rapid and efficient equilibration of the water phase both internally and with the overlying gas phase. Additionally, this removes the possibility of microbubbles within the water sampler.

Using the experimental protocol outlined here, accurate partitioning coefficients for noble gases were derived, and this approach also has application in the partitioning studies of other gases. The full set of results of this work have been synthesized and their implications for understanding natural CO_2-rich systems or underground CO_2 storage are described in a separate publication.[9]

[1]C. J. Ballentine, R. Burgess, and B. Marty, *Noble Gases in Geochemistry and Cosmochemistry*, Reviews in Mineralogy and Geochemistry (Mineralogical Society of America, 2002).
[2]Z. Zhou, C. J. Ballentine, R. Kipfer, M. Schoell, and S. Thibodeaux, Geochim. Cosmochim. Acta **69**, 5413 (2005).
[3]S. M. V. Gilfillan, B. S. Lollar, G. Holland, D. Blagburn, S. Stevens, M. Schoell, M. Cassidy, Z. J. Ding, Z. Zhou, G. Lacrampe-Couloume, and C. J. Ballentine, Nature **458**, 614 (2009).
[4]Z. Zhou, C. J. Ballentine, M. Schoell, and S. H. Stevens, Geochim. Cosmochim. Acta **86**, 257 (2012).
[5]M. J. Thoma, J. P. McNamara, M. M. Gribb, and S. G. Benner, J. Hydrol. **409**, 118 (2011).
[6]V. M. Heilweil, R. W. Healy, and R. N. Harris, J. Hydrol. **464**, 309 (2012).
[7]P. G. Burnard, R. Hu, G. Turner, and X. W. Bi, Geochim. Cosmochim. Acta **63**, 1595 (1999).
[8]M. A. Kendrick, G. Mark, and D. Phillips, Earth Planet. Sci. Lett. **256**, 328 (2007).
[9]O. Warr, C. A. Rochelle, A. Masters, and C. J. Ballentine, Geochim. Cosmochim. Acta **159**, 112 (2015).