

C-O-H speciation in piston-cylinder experiments

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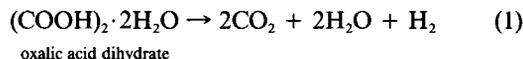
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ABSTRACT

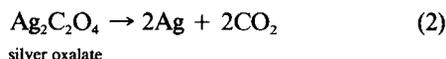
The effects of packing materials on H infiltration into sample capsules during piston-cylinder experiments has been examined using samples of oxalic acid dihydrate, silver oxalate, and pure carbon dioxide. Mass scans revealed that as much as several mole percent carbon monoxide, accompanied by H₂O, can result from a reaction between H and carbon dioxide in experiments using all three reactants. A measurable O isotopic shift was detected in carbon dioxide samples where carbon monoxide was detected. Traditional means for measuring C-O-H volatile composition at the end of piston-cylinder experiments will not identify this chemical change in the volatile composition and may result in erroneous determination of fluid composition. Glass and witherite packing materials effectively maintained a low f_{H_2} around the samples.

INTRODUCTION

As experimentalists continue to look at problems of fluid-rock interaction at intermediate pressure and temperature, it becomes increasingly important to be able to generate and maintain a fluid of known composition for the duration of piston-cylinder experiments. This paper is intended for those who conduct piston-cylinder experiments using CO₂- and H₂O-bearing fluids. The most common compounds used to generate these fluids are oxalic acid dihydrate and anhydrous oxalic acid for mixed CO₂-H₂O fluids and silver oxalate for pure CO₂ fluid (Holloway et al., 1968; Holloway and Reese, 1974). Our study only concerned the first and last of these compounds, which are assumed to react according to the equations



and



in environments of low f_{H_2} (Holloway et al., 1968). The breakdown of oxalic acid dihydrate theoretically would yield a 1:1 molar mixture of CO₂ and H₂O after the loss of H₂ from the sample volume (Eq. 1); silver oxalate would yield a pure CO₂ fluid on decomposition (Eq. 2). Problems of storage, dehydration, and H₂O adsorption can result, however, in fluids of nonstoichiometric compositions being produced from each of these compounds (i.e., Boettcher et al., 1973; Holloway and Reese, 1974).

The common method used for measuring the composition of the fluid phase of experimental charges is a pop-and-weigh technique. After an experiment, a capsule is recovered and weighed, punctured, reweighed, dried at ~100 °C for a short while, and then weighed for a final time. The first change in weight is attributed to the escape of CO₂; the second to H₂O loss. Boettcher (1984) modified this technique by freezing the capsule for 15 min prior to puncture to prevent excess H₂O loss in the vapor phase. In a series of experiments involving the hydrous oxalic acid, we found the composition of fluids determined varied from the ideal (Eq. 1) by as much as 15 mol%, indicating highly variable values of f_{H_2} in our experimental assembly. These deviations from ideality were much larger than those previously reported (i.e., Holloway et al., 1968). The purpose of this work was to determine the cause of the compositional variability in our samples and to establish a simple technique to maintain a stable fluid composition reproducibly.

EXPERIMENTAL METHODS

To examine the problem of variable fluid composition, three sets of experiments were conducted. The first two sets used powders, oxalic acid dihydrate or silver oxalate, to generate the fluid phase. In the third set of experiments, pure CO₂ was encapsulated directly as the fluid phase. The two powders were stored in a vacuum desiccator when not in use. A single batch each of oxalic acid dihydrate and of silver oxalate was used for all experiments. The oxalate was stored in a darkened container to avoid photodissociation. For the experiments labeled MS,

5–10 mg of oxalic acid or 15–20 mg of silver oxalate was loaded directly into either Pt or Au capsules. Most of the MS samples contained only one of these reagents, except

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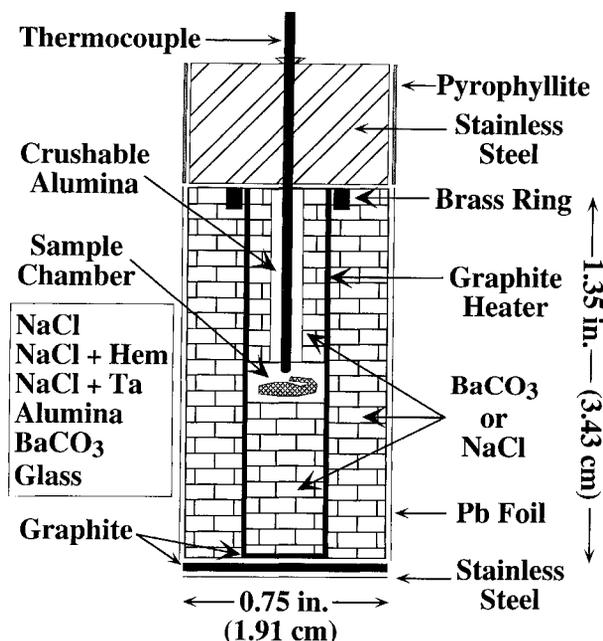


Fig. 1. Scale drawing of piston-cylinder cell used in high-pressure experiments. Box beneath the sample chamber label lists packing materials used around capsules.

for three oxalic acid experiments, which also held mineral phases (MS-13 and MS-17: magnesite and phlogopite; MS-51: phlogopite). For the experiments labeled BS, 25–200 μmol of isotopically-characterized CO_2 were dried and encapsulated cryogenically under vacuum (Rosenbaum, 1993). After reagents were loaded, the capsules were crimped and flame welded. Extreme care was taken to keep the capsules cold during the welding process to prevent reagent loss. CO_2 -bearing charges were partially immersed in liquid N_2 during welding; solid reagent samples were kept in cold H_2O .

Experiments were carried out in a piston-cylinder apparatus of the Boyd-England type (Boyd and England, 1960). Pressure was maintained to ± 150 bars and temperature to ± 1 $^\circ\text{C}$. Temperature was measured using a chromel-alumel thermocouple placed just above the sample capsule or a noble metal shield in intimate contact with the capsule. Given the errors introduced in temperature measurement by the relative positioning of sample, thermocouple, and graphite heater hot spot, the temperature of the sample was known to ± 5 $^\circ\text{C}$. A standard $\frac{3}{4}$ -in. piston-cylinder cell was used with either NaCl or BaCO_3 as the pressure medium (Fig. 1).

Three types of capsule assemblies were used. Single capsule experiments used either Pt or Au capsules of ~ 1.2 mm thickness. Double capsule assemblies were composed of a Pt inner capsule containing reagents and a Au outer capsule containing both the inner capsule and a hematite + H_2O mixture. Approximately 500 mg of hematite + H_2O mix was used in each double capsule sample to generate a hematite + magnetite + H_2O buffer. The final composition

of the buffers in the double capsule assemblies was checked at the end of each experiment. All three phases were present in the outer capsules of every experiment but MS-58, whose outer capsule visibly melted.

Powdered NaCl, BaCO_3 , Pyrex, soft glass, crushable alumina, pyrophyllite, and mixtures of 1:1 hematite to NaCl or hematite to BaCO_3 , 1:4 Ta to NaCl, and 1:9 Ta to NaCl or Ta to BaCO_3 were all used as packing materials (ratios are in weight proportions). Approximately 0.2–0.3 cm^3 of packing material was used in each experiment, creating a large, but finite, H-absorbing reservoir around the sample capsule (Fig. 1). Experimental conditions are summarized in Tables 1–3. Capsule weight was determined both before and after each experiment. Hematite and Ta often alloyed with the Pt capsules, especially at higher temperatures. Salt, carbonate, and glass were easily removed by soaking the capsule in H_2O , 6-N HCl, or 48% HF, respectively. Alumina proved impossible to remove completely, forming a solid ceramic casing about the sample.

Experiments were first pressurized to within $\sim 5\%$ of the final pressure, then heated to temperature and allowed to expand to final pressure. Quench times were usually < 1 min. After recovery, cleaning, and weighing, every capsule was mounted on a vacuum line and punctured. Volatiles condensable in liquid N_2 , primarily CO_2 and H_2O , were frozen into a cold finger while noncondensable gases were qualitatively measured using a pressure gauge on the vacuum line. A tesla coil was used for tentative identification of the noncondensable gases, since at the pressures of interest CO has a characteristic ionization color (light blue) different from that of N_2 (pink), the other major noncondensable gas in the product mixture. The tentative identification was later confirmed for several samples by mass spectrometric analysis of the noncondensable portion of the volatile package. The noncondensable gases were frozen into a sample tube using liquid He, then analyzed on a mass spectrometer by manually scanning the masses from 28 to 69 amu. CO, if present, yields a characteristic spectra at masses 28, 29, and 30. Although it is possible for small amounts of CO to be produced from the breakdown of CO_2 during mass spectrometric analysis, the absence of CO spectra in many CO_2 -bearing samples indicates this process was negligible in the current study.

The only phases left unfrozen in the line after the application of liquid He would be He and H_2 . Neither of these phases was detected in any of our experimental samples, though our gauge would not register less than ~ 5 – 10 μmol of these gases. The condensable gases were separated from each other cryogenically. CO_2 was measured by manometer and H_2O by pressure gauge; both measurements were checked against total weight loss. H_2O measurements were only semiquantitative on the vacuum line, because the pressure gauge was not calibrated for H_2O vapor. H_2O mole fractions were based on the difference between total weight and manometric measurements of the gaseous phases present. Given the uncertainties of the measurements, mole

TABLE 1. Oxalic acid dihydrate results at 800 °C and 8 kbar

MS no.	t (h)	PM*	Ox** (mg)	Yield† (%)	Mole fraction			Comments‡
					CO ₂	H ₂ O	CO	
13	1	S	5.00	n.d.	0.44	0.53	0.04	Mg + Phl, (s)
17	37	S	5.00	78.2	0.37	0.52	0.04	Mg + Phl, (s), 0.07 Mfr C
22	60	S	7.65	100.5	0.42	0.54	0.05	(s)
27	22	DC	8.04	98.0	0.52	0.48	0.00	
37	23	H	6.98	55.6	0.52	0.48	0.00	Au
39	23	S	7.76	48.3	0.46	0.52	0.02	Au
51	20	DC	4.23	95.3	0.55	0.45	0.00	Phl, 1000 °C, 15 kbar
54	23	H	6.71	99.6	0.56	0.44	0.00	
57	24	T	6.50	98.8	0.43	0.52	0.04	
64	25	T	7.33	43.0	0.42	0.53	0.04	Au, (s)

Note: all charges used NaCl cells and Pt capsules except where indicated.

* Packing material: S = NaCl; DC = double capsule assembly; H = hematite + NaCl (1:1 by weight); T = Ta + NaCl (1:9 by weight).

** Oxalic acid dihydrate.

† Percentage of volatiles recovered relative to theoretical yield. n.d. = not determined.

‡ Mg = magnesite; Phl = phlogopite; Au = Au capsule; Mfr C = mole fraction carbon; (s) = scanned on mass spectrometer.

fractions are considered accurate to ± 0.01 units. Carbon dioxide from direct encapsulation experiments was recovered as above, then analyzed isotopically. Our cryogenic separation would not separate CH₄ from CO₂, though no evidence of methane was seen in any of the samples analyzed on the mass spectrometer. The presence of CH₄ cannot be ruled out in the MS series; the isotope compositions of its samples were not determined. Isotope measurements were made on a Finnigan MAT Delta E mass spectrometer and are reported in standard stable isotope notation as $\Delta^{13}\text{C}$ and $\Delta^{18}\text{O}$ values, the difference in per mil (‰) between initial and final $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ values for each sample (cf. O'Neil, 1986). Stable isotope measurements were corrected for ¹³C and ¹⁷O contributions (after Craig, 1957). After the removal of fluids, all capsules were optically examined for the presence of graphite. Only one sample contained identifiable quantities of graphite (MS-17; Table 1).

DISCUSSION

Our experiments tested the effects of the pressure medium, packing material, and capsule material on fluid

composition. Both NaCl and BaCO₃ were used as pressure media with reasonable success. The composition of the outer sleeves (Fig. 1) did not affect the fluid composition of experimental samples. The material used for the inner core and packing was much more critical. In the CO₂ experiments, the capsule went into the press much like a small balloon containing liquid or vapor carbon dioxide. About half the experiments using NaCl inner parts failed because of in-situ shear stresses that ruptured the capsules. Two experiments suffering electrical shorts failed without ever having been heated, implicating initial pressurization as the cause of rupture. Little shearing was evident in experiments using BaCO₃ inner parts, probably because of the rigid behavior of the carbonate.

There was a definite mechanical difference between Au and Pt capsules in our experiments (Tables 1 and 2). All the charges in Au capsules lost approximately half their volatiles. The exact reason for this loss remains unknown. Although the volatiles must have been released to the immediate surroundings of the capsule, they do not appear to have had much effect on the overall ab-

TABLE 2. Silver oxalate results at 800 °C and 8 kbar

MS no.	t (h)	PM*	AgOx** (mg)	Yield† (%)	Mole fraction			Comments‡
					CO ₂	H ₂ O	CO	
24	25	DC	17.84	102.9	0.90	0.08	0.02	
28	19	S	19.62	104.0	0.84	0.12	0.04	(s)
38	23	S	17.32	26.9	1.00	0.00	0.00	Au
44	24	S	20.59	97.4	0.98	0.01	0.01	(s)
46	24	S	19.16	33.8	0.96	0.02	0.02	Au, (s)
53	24	H	14.69	96.8	0.81	0.09	0.10	wet day!
55	24	T	17.57	95.7	1.00	0.00	0.00	(s)
58	0.08	DC	16.46	91.4	0.97	0.02	0.01	outer capsule melted§
59	24	G	15.46	98.0	1.00	0.00	0.00	W
67	25	DC	17.02	98.9	1.00	0.00	0.00	
71	24	DC	16.80	97.2	1.00	0.00	0.00	
81	11	H	14.93	100.3	1.00	0.00	0.00	

Note: all charges used NaCl cells and Pt capsules except where indicated.

* Packing material: S = NaCl; DC = double capsule assembly; H = hematite + NaCl (1:1 by weight); T = Ta + NaCl (1:4 by weight); G = glass.

** Silver oxalate.

† Percentage of volatiles recovered relative to theoretical yield.

‡ Au = Au capsule; W = witherite cell; (s) = scanned on mass spectrometer.

§ Electrical failure.

TABLE 3. Carbon dioxide results at 12.5 kbar

BS no.	T (°C)	t (h)	CO ₂ (μmol)	Yield (%)	Δ ¹³ C (‰)	Δ ¹⁸ O (‰)	Δ ¹⁸ Oxs (‰)	CM	PM	Comments*
2	25	0	61.5	100.0	-0.07	-0.18	0.04	—	—	blank
3	25	0	61.5	99.9	0.01	0.03	-0.01	—	—	blank
1001	25	2184	102.7	100.4	0.09	-0.05	0.23	—	—	blank
1003	25	1968	109.5	88.0	0.00	0.07	-0.07	—	—	blank
1002	25	1968	117.8	100.4	0.09	0.03	0.15	—	—	blank
1501	25	144	150.9	85.9	-0.07	0.03	-0.17	—	—	blank
28	670	77.25	49.7	90.8	0.29	1.01	-0.43	S	W	(s), CO
17	670	95.5	55.7	94.4	-0.06	-0.05	-0.07	S	S	
16	670	64.5	69.4	98.7	0.11	0.44	-0.22	S	S	(s), CO
11	670	6	74.8	98.9	0.30	0.49	0.11	S	S	frozen twice
5	670	120	75.3	100.7	0.56	1.13	-0.01	S	S	
32	670	48	126.4	99.0	-0.03	0.08	-0.14	S	T	
49	700	72	120.3	8.5	-0.15	-0.13	-0.17	W	A	
65	700	72	148.6	9.6	0.12	-0.07	0.31	W	P	
63	700	72	188.2	99.5	0.31	0.55	0.07	W	W	
35	800	72	122.0	93.8	0.19	0.46	-0.08	S	W	IC:W, MF
68	900	72	49.7	98.8	-0.09	0.10	-0.28	W	SG	(s)
26	900	77.25	49.8	101.4	0.04	0.42	-0.34	S	W	
57	900	72	50.2	99.4	-0.17	0.20	-0.54	W	G	
23	900	77.25	51.0	99.7	0.05	0.49	-0.39	S	H	IC:H
20	900	77.25	51.4	100.0	-0.04	1.20	-1.28	S	S	(s), CO
33	900	72	101.3	99.8	0.12	0.17	0.07	S	W	IC:W
27	900	30	118.7	95.4	0.02	0.12	-0.08	S	W	IC:H
25	900	77.2	120.6	99.0	0.01	0.11	-0.09	S	W	(s)
54	1000	72	24.7	96.9	0.29	0.84	-0.26	W	W	
39	1000	72	99.0	18.7	0.01	0.03	-0.01	S	W	IC:W
36	1000	72	100.1	100.1	0.22	0.10	0.34	S	W	IC:W
43	1000	72	148.3	97.5	0.46	0.34	0.58	W	W	
41	1000	115.25	167.0	90.0	0.63	1.25	0.01	W	W	MF

Note: all charges in Pt capsules; $\Delta M = \delta M_i - \delta M_j$, where M = ¹³C or ¹⁸O; $\Delta^{18}\text{Oxs} = 2\Delta^{13}\text{C} - \Delta^{18}\text{O}$. CM = pressure cell material; S = NaCl; W = BaCO₃; PM = packing material; T = Ta + BaCO₃ (1:9 by weight); A = alumina; P = pyrophyllite; H = hematite + BaCO₃ (1:1 by weight); SG = soft glass; G = glass (Pyrex).

* One-bar blanks. MF = mass fractionated on sealing; (s) = scanned; CO = carbon monoxide; IC: = inner cell pieces.

sorbing capacity of the packing material (e.g., MS-27 and MS-37; Table 1). The capsules came out of the press visibly expanded and without any visible breaches, demonstrating that capsules can fail and subsequently reseal in the press. The data from Au capsule experiments have been renormalized assuming that the fluid lost did not appreciably change the composition of the remaining fluid. BS-39 is direct evidence that fluid loss can occur without appreciable change in the composition of the remaining reservoir. The final isotopic composition of the CO₂ in BS-39 remained unchanged in an isolated pocket, even though the pocket contained only 19% of the total amount of the gas originally present.

The nature of the material in the immediate environment of the sample capsule was critical for maintaining a stable fluid composition. The results of the oxalic acid dihydrate, silver oxalate, and CO₂ experiments are summarized in Tables 1, 2, and 3, respectively. In general, NaCl packing gave highly variable fluid compositions (Fig. 2). Although a few samples gave compositions that agreed well with Equations 1 and 2, most either failed or contained more H₂O than expected, usually accompanied by small amounts of carbon monoxide. MS-13 was especially interesting in this regard, as the mass scan of the condensable products showed an excess of mass 29 after accounting for the presence of carbon monoxide and air

(N₂) (Fig. 3). This excess was attributed to CHO⁺, suggesting that the oxalic acid dihydrate in the charge had not completely dissociated even after 1 h at 800 °C.

The use of Ta + NaCl mixtures as packing materials was not always effective (Fig. 2). For mixtures of Ta and NaCl in the weight ratio 1:9, there was no appreciable improvement over pure NaCl packing. H₂ was prevented from building up within samples by the presence of 20 wt% Ta, but Ta-Pt alloys formed, embrittling capsules and increasing failure rates. Hematite + NaCl mixtures were most effective on dry days, which suggests that their H₂ scavenging capacity may be saturated on days of high humidity, rendering them ineffective. Double capsule assemblies showed a similar behavior, though this was probably related to increased amounts of adsorbed H₂O on sample powders in the inner capsule. When soft glass or Pyrex completely enclosed a sample, it was effective at maintaining a low H₂ environment within the sample volume (Fig. 2).

The CO₂ experiments provided a very sensitive indicator of the presence of CO and H₂O in the samples. Formation of CO in a sample (Eq. 3; Holloway et al., 1968) would fractionate both C and O in the remaining reservoir, enriching it in ¹³C and depleting it in ¹⁸O. The generation of either graphite or CH₄ would affect only C; H₂O formation would affect only O. All three species

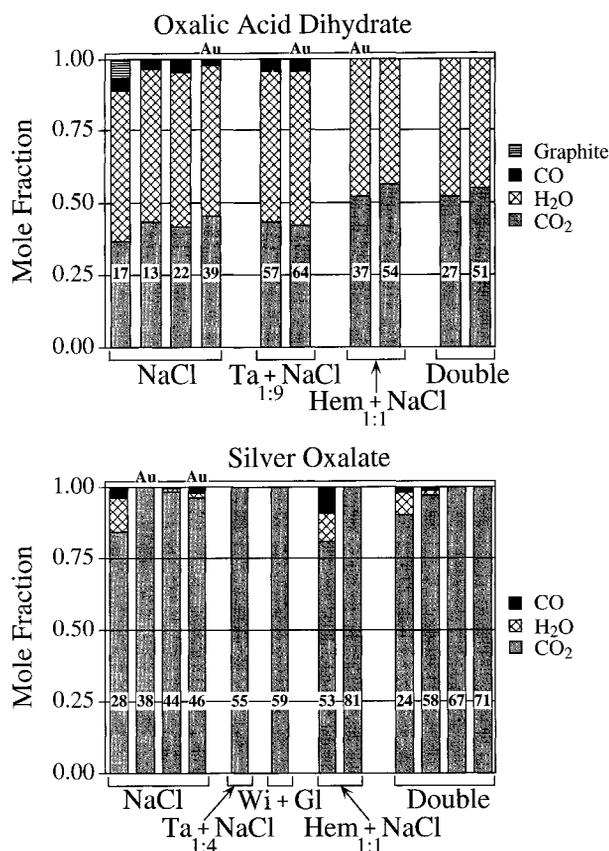
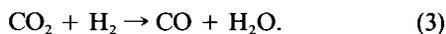


Fig. 2. Mole fraction of C, CO, CO₂, and H₂O in samples as a function of packing material (x axis) for experiments using oxalic acid dihydrate (top) and silver oxalate (bottom) powders as starting materials. Numbers correspond to data in Tables 1 and 2. Au indicates experiments in Au capsules; all others conducted in Pt capsules. Double indicates double buffer assembly using a Au outer capsule containing both a hematite + H₂O mixture and a Pt sample capsule. The expected theoretical composition of the fluid phase is 1:1 mole fraction CO₂ to H₂O for oxalic acid dihydrate and pure CO₂ for silver oxalate.

would leave the remaining CO₂ reservoir enriched in the heavier isotopes. The high temperatures and the small volumes of the products generated limit the isotopic shift resulting from these effects to <1‰ (Rosenbaum, unpublished data). Although CO, graphite, and CH₄ are relatively inert to isotopic exchange on quench, H₂O is not (Rosenbaum, 1993). Isotopic exchange in the CO₂-H₂O system would leave the CO₂ measurably enriched in ¹⁸O because O isotopic exchange is rapid (Mills and Urey, 1940; Rosenbaum, 1993) and the fractionation factors are large (Brenninkmeijer et al., 1983; Rosenbaum, 1993).



With the (2σ) error introduced during encapsulation, recovery, and measurement, Δ¹³C and Δ¹⁸O values should be within ±0.2‰ of zero if there was no change in isotope composition during an experiment. If not quantitative,

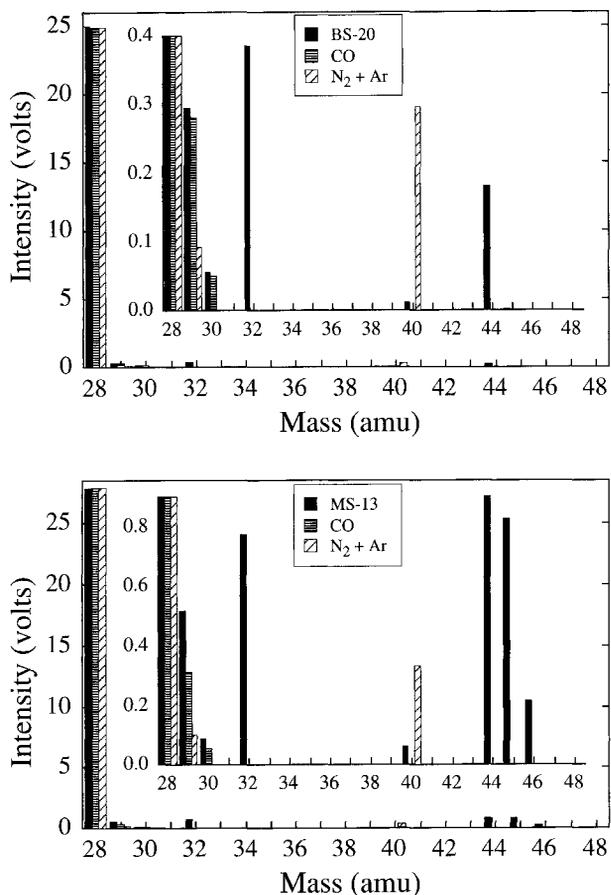


Fig. 3. Mass scan for samples BS-20 (top) and MS-13 (bottom) showing major peaks found in the mass range of 28–69 amu. Also shown are the synthetic peaks expected if mass 28 were wholly attributed to either CO or air (N₂ + Ar). Insets are expanded scale views showing the minor peak structure in each scan. The peak at mass 32 is due to an O₂ background in the machine. Both samples contain CO. The excess at mass 29 in MS-13 is attributed to the presence of CHO⁺, from incompletely reacted oxalic acid dihydrate.

the sealing procedure potentially can alter the isotope composition of the CO₂ reservoir. This type of mechanical mass fractionation results in a Δ¹³C:Δ¹⁸O ratio of ~1:2, as seen in BS-41 where only 90% of the starting CO₂ was encapsulated (Table 3). The column in Table 3 labeled Δ¹⁸O_{xs}, or ¹⁸O excess, is twice the Δ¹³C value less the Δ¹⁸O value. Values of Δ¹³C and Δ¹⁸O greater than or equal to ±0.2‰ and Δ¹⁸O_{xs} values near zero strongly suggest that mechanical mass fractionation has occurred. Positive Δ¹³C and Δ¹⁸O_{xs} values with near-zero Δ¹⁸O values are expected from the formation of graphite, CO, or CH₄ in the absence of H₂O. The net isotopic result of the formation of CO and H₂O in the sample is to generate measurable, negative Δ¹⁸O_{xs} values. Mass scans of several samples (BS-16, BS-20, BS-28) allowed positive identification of CO in samples with positive Δ¹⁸O and negative Δ¹⁸O_{xs} values (Table 3). The CO must have come

from reaction of the CO₂ with H₂ coming from either the capsule walls or the immediate environment around the capsule (Eq. 3).

The smallest CO₂ samples used were the most sensitive to the presence of H₂O on quench (Table 3). The smallest sample size that was successfully recovered unchanged was ~50 μmol. Sample sizes of ~100 μmol were much more robust (Table 3). No evidence of graphite formation was seen in any of the CO₂ samples. As mentioned earlier, most experiments conducted in salt cells failed. Of those that survived, only one, BS-17, an ~50-μmol sample heated to 670 °C, remained isotopically unchanged. BS-20, a sample of similar size heated to 900 °C, showed a marked change in its O isotope composition and contained CO (Fig. 3). The best results were achieved when samples were packed in soft glass, Pyrex, alumina, witherite, witherite mixed with 50 wt% hematite or 10 wt% Ta and contained at least ~50 μmol of CO₂.

Our results may be compared with the oxalic acid dihydrate decomposition experiments of Morgan et al. (1992) conducted in silica glass capsules in cold seal vessels. In their study, CO formed by the decomposition of oxalic acid dihydrate and persisted because of the kinetic barriers to graphite and methane formation (Morgan et al., 1992). Their samples that had significant H₂ loss from the capsules showed an increase in CO₂ concentration at the expense of both H₂O and CO concentrations. Our pure CO₂ experiments conclusively demonstrate that H₂ can infiltrate into the sample volume and react to produce both CO and H₂O (Eq. 3). The CO observed in the oxalic acid experiments is probably the result of the process observed by Morgan et al. (1992), caused by the low H-absorbing capacity of the environment around the samples. The CO and excess H₂O found in the oxalate charges are most likely due to a combination of H₂ infiltration and reaction and the presence of small, variable amounts of adsorbed moisture.

SUMMARY

The quantitative, in-vacuo technique used for CO₂ encapsulation in our experiments, used successfully to encapsulate CO₂ + H₂O mixtures (Rosenbaum, 1993), may prove a valuable technique for generating fluids of known CO₂-H₂O ratios in piston-cylinder experiments. The experimental data presented in this study show that the composition of CO₂-H₂O fluids produced in piston-cylinder experiments is highly dependent on the H-absorbing capacity of the material in the immediate environment of the sample capsule. Even when precautions are taken to keep starting materials dry, if the H-absorbing capacity of the packing material is saturated, CO₂ tends to react with H to produce CO and H₂O. Standard pop-and-weigh techniques are not sensitive enough to detect

this shift in volatile composition and may result in the determination of erroneous compositions. In pure CO₂ samples, O isotopes can be used to identify the presence of small quantities of H₂O. Double capsule assemblies with sufficient H-absorbing capacity maintain their fluid compositions but are time consuming and expensive to use. Soft glass, Pyrex, and witherite packing materials are inexpensive and easily employed alternatives to the double capsule technique for maintaining a low f_{H_2} in the immediate sample environment.

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