

### Supplementary data

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2 Three sources of CO<sub>2</sub> were used in the experiments: hydrous oxalic acid,  
3 H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>•2H<sub>2</sub>O (HOX), silver oxalate, AgCO<sub>2</sub>, (AgOX), and silver carbonate (Ag<sub>2</sub>CO<sub>3</sub>).  
4 For fluid mixtures up to X<sub>CO<sub>2</sub></sub> of 0.5, reagent HOX was used with varying amounts of  
5 H<sub>2</sub>O. The HOX (Fisher Certified) is in the form of limpid crystals of about 10 μg, which  
6 could be loaded individually to achieve a desired fluid mass. This material generates a  
7 fluid mix of molar proportions 2H<sub>2</sub>O:2CO<sub>2</sub>:H<sub>2</sub> during an experiment. The H<sub>2</sub> must be  
8 purged by buffering at high oxygen fugacity (*f*<sub>O<sub>2</sub></sub>). Experiments in this laboratory and  
9 elsewhere (Rosenbaum and Slagel 1995) have shown that HOX reliably generates a 50  
10 mol % CO<sub>2</sub> mixture with H<sub>2</sub>O if buffered externally with hematite-magnetite-H<sub>2</sub>O, with  
11 the Pt capsule acting as a H<sub>2</sub>-permeable membrane. The principal disadvantage of this  
12 method is that a welded Pt inner capsule must be used to contain the experimental charge,  
13 since most of the large capsule volume is filled with the buffer mix (totaling about 100  
14 mg). This limits the CO<sub>2</sub>-H<sub>2</sub>O fluid mass to only about 5 mg and the crystal mass to 0.5  
15 mg. For high CO<sub>2</sub> fluids the quartz weight loss would be too small to measure with the  
16 buffered capsule method.

17 Experiments with >50 mol % CO<sub>2</sub> used AgOX as a CO<sub>2</sub> source. AgOX is a  
18 conveniently loaded material (small coherent pellets of powder), but it decomposes at  
19 low *T* and cannot be oven dried. Previous work in this laboratory (Ferry et al. 2002) has  
20 shown that our material (ICN batch #23962-A) has a small amount of adsorbed H<sub>2</sub>O, and,  
21 moreover, the slightly gray color indicates probable slight photodecomposition to Ag  
22 metal. For these reasons the volatile yield of AgOX had to be calibrated by weight loss  
23 measurements. An aliquot of about 50 mg of AgOX with or without additional H<sub>2</sub>O was

24 weighed into a segment of the large Pt tube and welded without significant mass loss.  
25 This charge was run at the same conditions as all experiments (800 °C, 10 kbar) for  
26 periods of up to two days and quenched in the usual manner. The retrieved capsules were  
27 inflated due to CO<sub>2</sub> pressure and showed no mass loss. A capsule was punctured with a  
28 tiny hole under liquid N<sub>2</sub> using a sharp needle, and then placed in a refrigerator freezer  
29 for up to one hour. This procedure is necessary to avoid spraying of liquid H<sub>2</sub>O upon  
30 puncture. The capsule was weighed at intervals until a constant weight (the “plateau  
31 weight”, Table S1) was attained, which usually took about 1/2 hr. Comparison weighings  
32 with liquid H<sub>2</sub>O showed that the puncture hole was too small to allow weighable  
33 evaporation of liquid water at room temperature. The plateau weight was taken to  
34 indicate, by subtraction, the CO<sub>2</sub> yield. The perforated capsule was then heated at 115 °C  
35 for 15 minutes followed by 15 minutes at 350 °C. The additional weight loss was taken as  
36 the total H<sub>2</sub>O yield. Four such volatile loss experiments were performed (Table S1). The  
37 runs consistently showed that a small fraction of the expected volatile yield of the AgOX  
38 was actually H<sub>2</sub>O. They also revealed a small additional CO<sub>2</sub> mass deficiency, which  
39 presumably results from photodecomposition. A typical gas yield analysis is shown in  
40 Fig. S1. The four yield tests were averaged to obtain corrected CO<sub>2</sub> and H<sub>2</sub>O yields: 95.5  
41 wt% of the expected CO<sub>2</sub> yield, based on AgCO<sub>2</sub> stoichiometry, and 2.79 wt% of the  
42 expected CO<sub>2</sub> yield, respectively.

43 A third starting fluid source consisted of silver carbonate (Ag<sub>2</sub>CO<sub>3</sub>: Aesar  
44 99.999% certified) and HOX in equimolar proportions, so that the excess H<sub>2</sub> of the HOX  
45 and the excess O of the Ag<sub>2</sub>CO<sub>3</sub> were compensated. A serious disadvantage of this CO<sub>2</sub>  
46 source is the very large amount of Ag and the relatively small amount of CO<sub>2</sub> yielded by

47 the Ag<sub>2</sub>CO<sub>3</sub>. For reasons not clear, the quartz crystals sometimes became coated with Ag  
48 metal and could not be easily cleaned. A few runs were made with the quartz crystal  
49 protected by a perforated inner Pt capsule, but in these experiments the perforations were  
50 plugged by Ag metal, and the crystals yielded anomalously low weight losses compared  
51 to results based on other methods. These manifestly underequilibrated runs are not  
52 reported in Table 1, text. Thus, the Ag<sub>2</sub>CO<sub>3</sub> + HOX mix was less satisfactory as a CO<sub>2</sub>  
53 source at high CO<sub>2</sub> mole fractions.

54 Activities of H<sub>2</sub>O and SiO<sub>2</sub> from this study and others at different *P* and *T* are  
55 tabulated in Table S2, and plotted in Fig. 2C, text.

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#### References cited

58 Anderson, G.M. and Burnham, C.W (1965) The solubility of quartz in supercritical  
59 water. American Journal of Science, 263, 494–511.

60 Ferry, J.M., Newton, R.C. and Manning, C.E. (2002) Experimental determination of the  
61 equilibria: rutile + magnesite = geikielite + CO<sub>2</sub> and zircon + 2magnesite =  
62 baddeleyite + forsterite + 2CO<sub>2</sub>. American Mineralogist, 87, 1342–1350.

63 Rosenbaum, J.M. and Slagel, M.M. (1995) C-O-H speciation in piston-cylinder  
64 experiments. American Mineralogist, 80, 109–114.

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#### Figure caption

67 **Figure S1.** Volatile yield from silver oxalate decomposition in a welded Pt capsule at 800  
68 °C and 10 kbar (Run 32, Table S1). The quenched, inflated capsule was punctured  
69 under liquid N<sub>2</sub> and left in a freezer for 1 hr before weighing began.

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**Table S1.** Volatile yields of silver oxalate (AgOX).

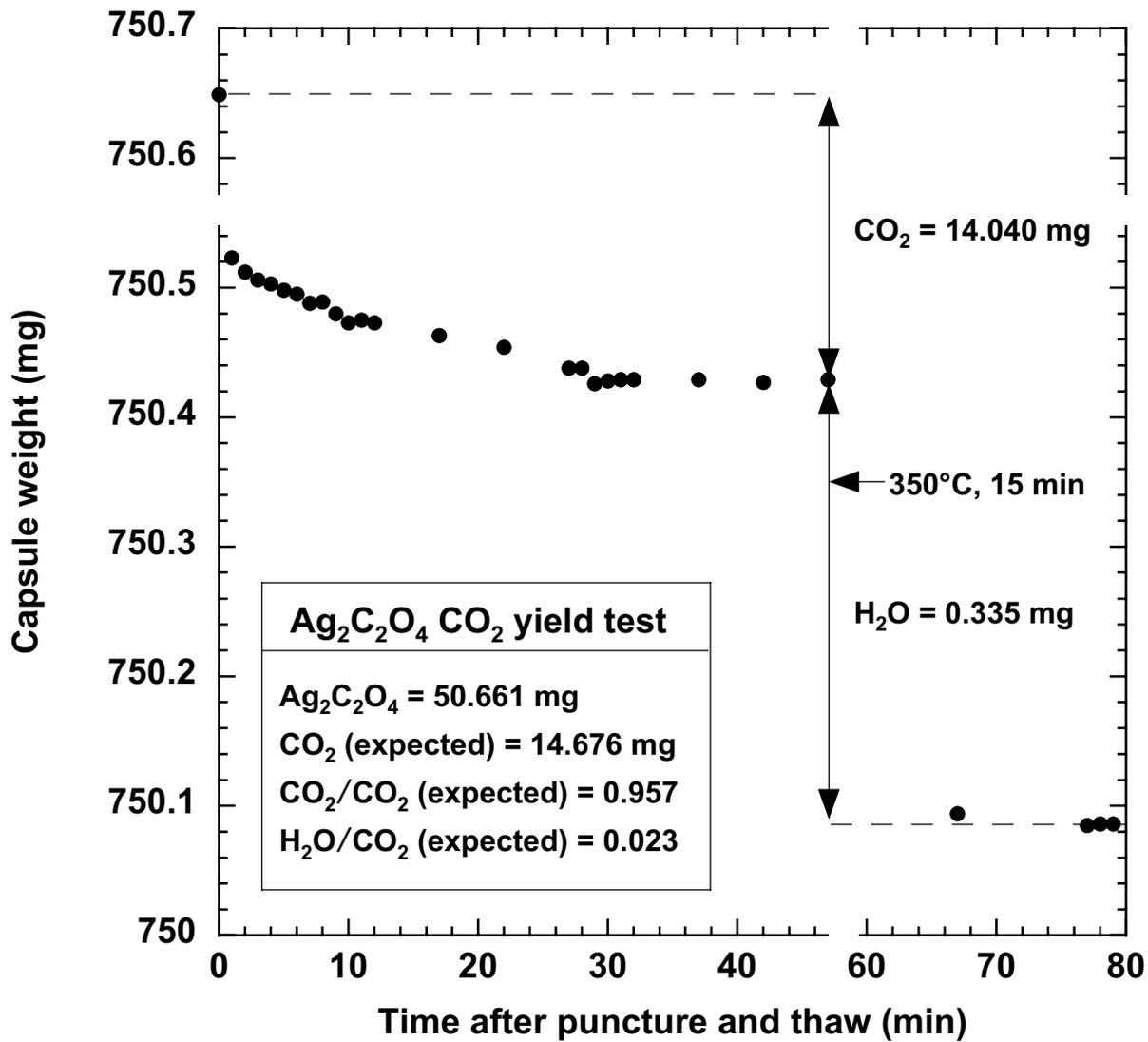
Expt. no.	Run Time (hr)	AgOX (mg)	H <sub>2</sub> O (mg)	Capsule Out (mg)	Capsule change (mg)	Plateau weight (mg)	Dried Weight (mg)	% CO <sub>2</sub> (of nominal CO <sub>2</sub> )	% H <sub>2</sub> O (of nominal CO <sub>2</sub> )
32	8	50.661		764.469	-0.020	750.427	750.086	95.66(2)	2.32(2)
33	13	46.887		713.761	-0.028	700.873	700.396	94.86(2)	3.51(2)
34	9	46.260		732.112	-0.043	719.312	718.950	95.49(2)	2.70(2)
42	40	51.842	1.961	955.046	+0.005	940.620	938.262	96.03(2)	2.64(3)
Ave:								95.51(24)	2.79(25)

Weighing uncertainty is 2  $\mu$ g ( $1\sigma$ ); parenthetical entries are  $1\sigma$  or 1 standard error in last digit(s).

**Table S2.** Parameters derived from selected experimental studies of quartz solubility in H<sub>2</sub>O-CO<sub>2</sub>.

$X_{\text{H}_2\text{O}}$	$\log a_{\text{H}_2\text{O}}$	$X_{\text{SiO}_2}$	$\gamma_{\text{SiO}_2}$	$a_{\text{SiO}_2}$	$\log \frac{a_{\text{SiO}_2}}{a'_{\text{SiO}_2}}$	Notes
Novgorodov (1975), 700°C, 5 kbar, $K_{md} = 242$						
1	0	7.12E-03	0.413	2.94E-03	0	
0.91	-0.036	4.60E-03	0.482	2.22E-03	-0.122	
0.88	-0.046	3.94E-03	0.508	2.00E-03	-0.167	
0.87	-0.050	3.23E-03	0.541	1.75E-03	-0.225	
0.81	-0.071	2.61E-03	0.578	1.51E-03	-0.290	
0.72	-0.104	1.79E-03	0.643	1.15E-03	-0.408	
0.55	-0.181	6.62E-04	0.796	5.27E-04	-0.746	
0.527	-0.194	6.70E-04	0.795	5.33E-04	-0.742	
0.513	-0.202	7.50E-04	0.779	5.84E-04	-0.701	
0.503	-0.208	5.58E-04	0.819	4.57E-04	-0.808	
0.50	-0.210	5.28E-04	0.826	4.36E-04	-0.829	
0.495	-0.213	5.26E-04	0.826	4.34E-04	-0.830	
0.32	-0.359	2.60E-04	0.898	2.33E-04	-1.100	
Novgorodov (1975), 700°C, 3 kbar, $K_{md} = 309$						
1	0	4.79E-03	0.436	2.09E-03	0	From AB65
0.91	-0.036	2.79E-03	0.525	1.47E-03	-0.154	
0.77	-0.090	1.39E-03	0.643	8.97E-04	-0.367	
0.50	-0.225	3.70E-04	0.839	3.11E-04	-0.828	+graphite
0.36	-0.339	1.74E-04	0.911	1.58E-04	-1.120	+graphite
0.33	-0.371	1.51E-04	0.921	1.39E-04	-1.176	
0.23	-0.507	9.07E-05	0.949	8.61E-05	-1.385	+graphite
Walther and Orville (1983), 600°C, 2 kbar, $K_{md} = 250$						
1	0	2.17E-03	0.604	1.31E-03	0.000	From AB65
0.977	-0.010	1.91E-03	0.626	1.19E-03	-0.040	
0.964	-0.015	1.67E-03	0.649	1.08E-03	-0.083	
0.902	-0.039	1.25E-03	0.696	8.73E-04	-0.176	
0.889	-0.044	1.20E-03	0.703	8.43E-04	-0.191	
0.837	-0.063	9.49E-04	0.740	7.02E-04	-0.271	
0.702	-0.115	4.70E-04	0.836	3.93E-04	-0.523	
0.689	-0.121	3.81E-04	0.859	3.27E-04	-0.602	
Shmulovich et al (2001), 800°C, 9 kbar $K_{md} = 252$						
1	0	2.16E-02	0.261	5.63E-03	0	From S06
0.7027	-0.102	4.47E-03	0.443	1.98E-03	-0.455	
0.6482	-0.121	3.35E-03	0.482	1.62E-03	-0.542	
0.4991	-0.189	1.86E-03	0.555	1.03E-03	-0.737	
0.4992	-0.189	1.53E-03	0.588	9.02E-04	-0.796	
0.8354	-0.059	8.87E-03	0.355	3.15E-03	-0.253	
This study, 800°C, 10 kbar, $K_{md} = 229$						
1	0	2.20E-02	0.269	5.92E-03	0	From NM00
0.9234	-0.030	1.46E-02	0.319	4.54E-03	-0.116	
0.8216	-0.062	8.53E-03	0.394	3.18E-03	-0.270	
0.8163	-0.064	8.96E-03	0.387	3.27E-03	-0.257	
0.6663	-0.111	3.83E-03	0.522	1.84E-03	-0.509	
0.6599	-0.113	4.05E-03	0.513	1.90E-03	-0.493	
0.5748	-0.145	3.21E-03	0.552	1.59E-03	-0.571	
0.5002	-0.180	1.81E-03	0.650	1.05E-03	-0.753	
0.5000	-0.181	1.72E-03	0.658	1.01E-03	-0.768	
0.4435	-0.213	1.27E-03	0.709	7.94E-04	-0.873	
0.4379	-0.217	1.09E-03	0.732	7.11E-04	-0.920	
0.3696	-0.266	6.49E-04	0.807	4.65E-04	-1.105	
0.3180	-0.314	4.26E-04	0.857	3.26E-04	-1.259	
0.2528	-0.391	1.88E-04	0.926	1.59E-04	-1.570	

Abbreviations: AB65, Anderson and Burnham (1965); NM00, Newton and Manning (2000); S06, Shmulovich et al (2006).  $K_{md}$  calculated using Eq. 5, text.



Newton & Manning, Fig. S1