

EFFECT OF CARBON MONOXIDE ON LIQUIDUS TEMPERATURES OF SILICATE MELTS AT 1-ATM PRESSURE. R. O. Colson¹, E. Hay, A. Larson, and A. Cota, ¹Minnesota State University Moorhead, Moorhead MN 56563, colson@mnstate.edu.

Introduction: Carbon monoxide gas has a significant and previously unrecognized influence on phase equilibria at one-atmosphere pressure. The liquidus temperatures of some silicate compositions vary by more than 100°C as a function of CO in the gas phase.

The influence of CO on phase equilibria and partitioning is poorly understood even though f_{O_2} conditions expected on the Moon are consistent with a significant fraction of the gas being CO. CO was likely a significant contributor to firefountaining on the Moon [1, 2, 3]. Typically, it is assumed that solubility of CO at low pressure is insignificant and thus CO has little effect on phase equilibria and partitioning. This assumption has seemed sound since CO solubility has been reported to be negligible up to 2GPa in some compositions [4, 5]. However, other workers have found CO solubilities up to a few percent in the pressure range of 2-3 GPa [6]. Vesiculation in quenched experimental samples run in CO-rich atmospheres has suggested that CO or some other reduced C species may dissolve in the melt and exsolve during quench [7, 8, 9]. In the present experiments, bubbles are observed in Fe-free samples run at 1 atm pressure in a CO-rich atmosphere. Bubbles occur in the interior of the bead and not attached to surfaces of crystals, the edge of the bead, or the sample assembly, suggesting they formed during the quench.

Experimental: Because these experiments were intended to test whether CO gas has an effect on phase equilibria that can't be accounted for by changing oxidation states of iron in the melt, we chose to do them in an Fe-free system to avoid the ambiguities that arise if Fe valence, as well as CO, is influencing the system. Compositions were mixed from reagent-grade silicic acid, Al_2O_3 , $CaCO_3$, and MgO. Correction for water content in the reagents was made on the basis of previous drying and weighing. Mixtures were ground under alcohol with an agate mortar and pestle for twenty minutes or more to insure homogeneity. Compositions are given in Table 1.

Samples were mounted on Pt loops and run in 1-atm gas mixing furnaces. T was controlled to within ± 2 degrees and measured with a type-S Pt-Rh thermocouple. Samples were run in various mixtures of CO_2 -CO gas controlled by gas flow meters.

Samples were air quenched and examined optically under a microscope for olivine crystals in an effort to constrain the liquidus temperature. Because the samples were Fe-free, even very small crystals were easily

seen. Repetitions suggested that this method had an uncertainty of less than 4°C.

To minimize the problem of failure of crystals to nucleate or melt exactly at the liquidus, experiments were reversed as follows. If crystals were present in the glass, the temperature was progressively raised until no crystals were seen. If no crystals were seen, then the temperature was progressively lowered until crystals were seen.

Table 1. Target compositions

	Comp 1	Comp 2	Comp 3	Comp 4
	PtIp-SCMA-7-1	PtIp-SCMA-10-2	PtIp-SCMA-10-3	PtIp-SCMA-10-4
SiO ₂	57.5	52.7	50.0	46.7
Al ₂ O ₃	7.2	10.0	10.0	10.0
MgO	31.3	35.3	21.1	28.2
CaO	4.0	2.0	18.8	15.1

Experiments were equilibrated in the furnace for 45 minutes to 48 hours. Durations less than 45 minutes were often inadequate for achieving equilibrium results, particularly near the liquidus temperature. For experiments run in CO_2 but that had previously been exposed to a CO-rich atmosphere, 24-48 hours were required for equilibration. Equilibrium was presumed when leaving the sample in the furnace for progressively longer times no longer resulted in any experimental differences.

Results: Results for compositions 1 and 2 are shown in Figs. 1 and 2. The liquidus temperatures for these compositions are shifted by as much as 130°C by the presence of CO at 1 atm pressure. Such a large effect can be expected to influence magma evolution and partitioning under f_{O_2} conditions of lunar magmatism. The magnitude of the effect can be understood by considering how much the presence of CO changes activity coefficients. Considering a simplified reaction:



$$\Delta G = \Delta G^\circ - RT \ln K$$

where K = the activity of Fo(solid) divided by activity of Fo(melt), and $\Delta G=0$ at the liquidus T.

Taking ΔG° from [10] for the two cases: 1) composition 1 in CO_2 with liquidus of 1508°C and 2) the same composition in 90% CO with liquidus of 1625°C yields:

$$0 = \Delta G^\circ_{1508} + RT \ln K = -2523J + RT \ln K_{in CO_2}$$

and

$$0 = \Delta G^{\circ}_{1625} + RT \ln K = 1087J + RT \ln K_{in CO}$$

$$K_{in CO_2} = 1.18, \text{ and } K_{in CO} = 0.93$$

This shows that presence of CO changes the ratio of activities of forsterite in solid and melt by 26%. Such a variation in activity may influence other components as well, affecting a variety of phase relations and partitioning reactions.

The influence of CO on phase relations is not straightforward. Experiments done in other compositions with lower liquidus temperatures resulted in no measurable effect of CO. For example, in a third composition (lower SiO₂, higher CaO), liquidus T in CO₂ was bracketed between 1432°C and 1434°C. The liquidus in the presence of 96% CO was bracketed between 1430°C and 1435°C, basically identical.

In addition, a fourth composition appeared to show the opposite effect of CO, with the fraction of melt crystallized decreasing with increasing CO. We have not yet bracketed liquidus temperatures in this composition.

The relationship between liquidus T and fraction CO is not linear, as shown in Fig. 1. This might indicate that CO is not the species directly influencing the liquidus T. For example, $a(CO)_x$, aC , and aSi^{2+} will increase non-linearly with increasing CO. Alternatively, the non-linear nature could indicate that the effect of CO is strongly temperature-dependent, increasing with increasing T. This might explain the lack of effect seen for the third composition (lower liquidus) and the stronger effect seen in the second composition (higher liquidus-Fig. 2). Another qualitative observation that suggests that there might be a temperature dependence is that the fraction of crystallization does not increase as quickly below the liquidus T in the CO-rich atmosphere as in the CO₂. This qualitative observation is illustrated in Fig. 3. Figure 3 shows that the effect of CO is more complex than simply shifting the liquidus.

Other workers have reported that methane can expand the Fo stability field [6, 11]. They interpreted this as due to depolymerization of melt. CO might have a similar effect. However, based on our experiments, the CO must be either increasing the activity of forsterite in the melt or decreasing its activity in the solid. It might be influencing both to varying degrees, explaining why the effect of CO is reversed in some compositions. There is no iron present in our experiments, so the olivine is austensibly pure forsterite. However, if CO dissolves in the solid phase it could act as a dilutant, lowering forsterite activity.

Conclusions The main conclusion of this study is that further investigation of the effect of CO (and/or fO₂) on silicate melts is warranted. CO (and/or fO₂)

changes the liquidus temperature in silicate melts of some compositions by more than 100°C. This effect is observed at fO₂ values expected for the Moon and thus has potentially significant implications for many problems in lunar differentiation and volcanism.

References: [1] Fogel, R.A. and Rutherford M J (1995) [2] Nicholis M G and Rutherford M J (2005) LPSC XXXVI, 1726. Geochim. Cosmochim. Acta, 59, 201-215 [3] Rutherford M J and Papale P (2003) LPSC XXXIV, 1322. [4] Pawley A. R. Holloway J. R., and McMillan P. F. (1992) Earth Planet Sci Lett 110, 213-225. [5] Thibault Y. and Holloway J. R. (1994) Contrb. Min. Pet 116, 216-224. [6] Eggler D. H., and Baker D. R. (1982) Adv. Earth Planet Sci 12, 237-250. [7] Colson R. O. (1993) LPSC XXIV 321-322. [8] Nesheim T, Colson R. O. Cota, A., Larson, A. Rock, J and Johnson C (2007) LPSC XXXIIX, 1719. [9] Everman R L A and Cooper R F (2003). J. Am Ceram. Soc. 86, 487-494. and personal comm. Everman (2004). [10] Barin I (1989) Thermochemical data of pure substances. VCH Verlagsgesellschaft. [4] [11] Green D. H. Falloon T J and Taylor W. R. (1987) in Magmatic Processes" physicochemical principles (ed B O Mysen) 139-154.

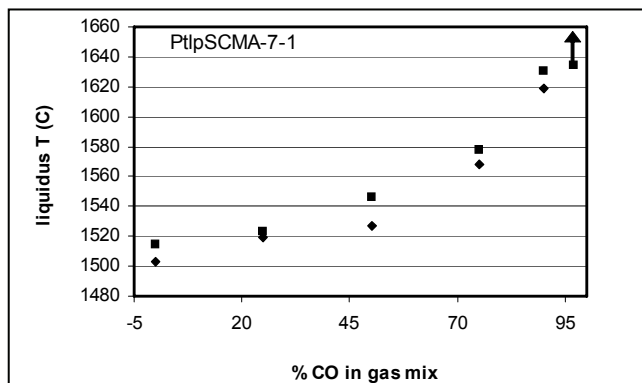


Fig. 1. Liquidus temperature vs fraction CO in a CO₂-CO mixture. Diamonds = silicate melt was decreased in T until crystals were seen. Squares = crystal-bearing melt is raised in T until the crystals disappeared. Arrow = melting T not achieved.

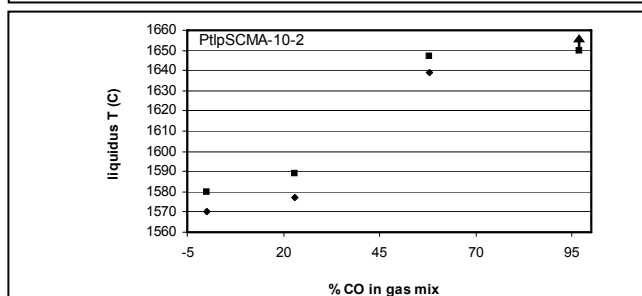


Fig. 2. Symbols as in Fig. 1

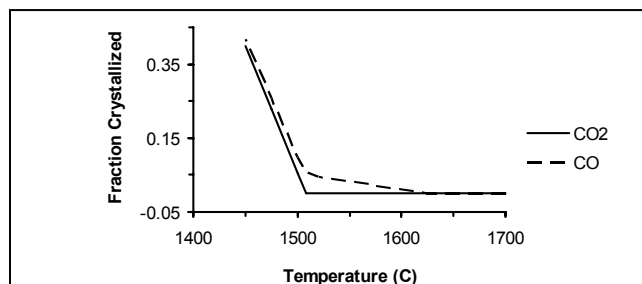


Fig. 3. The fraction of melt crystallized does not increase as sharply below the CO-liquids as below the CO₂ liquidus