Does fO2 influence reversible silicate melting without redox-active cations?

David Walker a,b,1, Shuo Ding c, and Yves Moussallam a,b

Lin et al. (1) report variable freezing-point depressions in an Fe-free basalt composition in controlled-cooling crystallization experiments performed at a range of fO2 in CO2–CO mixed gases and in air. They claim that fO2 strongly condition the melting behavior of planetary materials without redox-active cations, even though they performed no melting experiments. In contrast, we show that the melting points of standard substances, diopside, lithium metasilicate, and gold, are insensitive to fO2. We also show that the reversible liquidus for an Fe-free basalt composition resembling Lin et al.’s is insensitive to fO2. Controlled cooling experiments (at rates of 0.9 °C/h, 4 °C/h, and 600 °C/h) of our Fe-free mid-ocean ridge basalt composition in air also show no undercooling below the reversible liquidus, contrary to Lin et al. (1). Because we observe minimal supercooling in Fe-free basalt at any explored cooling rate, the observations of Lin et al. (1), that we fail to reproduce, are hard to understand as cooling rate controlled kinetic effects, but they may be artifacts of pyrometry problems. Either way, they do not lead to any important changes in our understanding of planetary melting. Claims of new planetary melting regimes are unfounded. The answer to the title question is no.

It has been known for some time (2) that silicate melting and crystallization can be complicated by kinetics and that melting and crystallization are not just the reverse of each other. The methods developed to unravel the complications include the quenching method and bracketing of phase-change reversals (3). "Boundaries" for melting or crystallization outlined without reversals and bracketing in both directions may be of little value in determining equilibria. The question of whether it is important to establish equilibrium depends on context. For example, in kinetic studies of a sluggish crystallization process, equilibrium is only of referential interest. However, studies at laboratory time scale without reversals and bracketing are of underestimated relevance to natural melting phenomena that occur on geological time scales. Reversible phenomena are of more proven relevance to problems of planetary melting.

The issue of reversibility is central to evaluating the recent study by Lin et al. (1). They crystallized an Fe-free basalt composition at three fO2 values at a controlled cooling rate of 5 °C/h and held the product at the target temperature for 36 h. Their highest fO2 was in air, and lower ones down to the iron-wüstite (IW) buffer were generated by mixing CO and CO2 gas. Their crystallizations began from a liquid state and were stopped for inspection at various quench temperatures below the starting liquid temperature. The appearance temperatures of crystals were delineated by observation of crystal assemblage with quenching temperature. The appearance temperatures on cooling were not reversed and bracketed by melting experiments recording the disappearance temperatures upon heating of the crystals. Based on the unreversed liquidus, Lin et al. (1) claim a freezing-point depression of the order of 100 °C in air compared to CO/CO2 = IW. Given there were no cations present whose variable valence state could cause such a change in the crystallization behavior by conventional means, Lin et al. (1) offer an unconventional anionic explanation. However, the phase appearance boundaries and phase percent contours presented by Lin et al. (1) are only lower bounds on the equilibrium positions of the liquidus and phase appearance temperatures during crystallization. That is, their claim of an effect on melting behavior was based not on experiments which fixed the melting points but on crystallization experiments which only gave lower bounds on the freezing points. Further testing of these extraordinary claims is necessary.

Reference Substance Behavior

If fO2 can have a major effect on the melting behavior of metasilicate-like Fe-free basalt, it might also be observable in the melting of simpler reference substances. Ca–Mg metasilicate (diopside, CaMgSi2O6) and lithium metasilicate (Li2SiO3) are reference standards for thermocouple calibration by melting point determination. We use them, as well as gold, to calibrate our furnaces and their thermocouples, in air. If the fO2 effect on melting is real, we might expect to see a change in the melting points of these standards with respect to air by application of CO/CO2 to reach the IW buffer during their melting. Table 1 gives the brackets on the melting points of these standard substances in air and at CO/CO2 = IW. All experiments in this study were run in a single DelTech DT-31-VT-OS furnace lined with an impervious Al2O3 tube of 1.25-inch internal diameter, within which are variable gas atmospheres (air or CO/CO2 mixtures) whose fO2 was monitored with a CSIRO ZrO2 (doped with yttria) electrochemical probe that included a new type S (Pt/Pt10Rh) thermocouple. The T °C entries in Table 1 follow directly from the room-temperature-compensated voltages on the new type S thermocouple within the fO2 probe. The melting points determined by quenching with bracketing agree with the International Practical Temperature Scale–based (4) values of 1,064, 1,203, and 1,391 °C for Au, lithium metasilicate, and diopside, respectively, within error. Thus, no secondary corrections for thermocouple aging...
are required for this series of experiments. (Au is not bracketed in the reversal sense because its abrupt melting point is determined by direct visual observation in the furnace of a strip abruptly transforming to a bead during very slow heating.) Fig. 1 indicates that there is no $f$O$_2$ effect on the melting or crystallization of these reference pure substances.

### Fe-Free Basalt Behavior

We also evaluated the liquidus behavior in air of an Fe-free basalt to see whether a complex composition with a large melting interval might achieve Lin et al.’s (1) freezing-point depression. It does not. Our composition (SiO$_2$ 51.22; TiO$_2$ 1.77; Al$_2$O$_3$ 17.14; MgO 8.68; CaO 19.99; Na$_2$O 2.45; K$_2$O 0.10) loosely resembles that of Lin et al. (1). Glass was prepared from mixed oxides and carbonates by two 2-h fusions at 1,350°C in a Pt crucible in air with intermediate crushing. A fully crystalline version was prepared from a mixture of crystals in the controlled cooling crystallization in air of Lin et al. (1).

| Entry | Temperature °C | log fO$_2$ | Gas | Minutes | Start | Product |
|-------|----------------|------------|------|---------|-------|---------|
| 27    | 1,392          | −0.7       | Air  | 60      | Crystals | Glass   |
| 10    | 1,391          | −0.7       | Air  | 30      | Liquid | Crystals & glass |
| 25    | 1,393          | −9.6       | CO/CO$_2$ | 30 | Crystals & liquid | Glass* |
| 28    | 1,390          | −9.8       | CO/CO$_2$ | 60 | Liquid | Crystals & glass |

**Table 1. Experimental results**

**Fig. 1.** Temperatures of melting/freezing as a function of $f$O$_2$. Diopside, Li$_2$SiO$_3$, and Au melting points are not sensitive to $f$O$_2$. Neither is a generic Fe-free basalt investigated here by phase appearance reversals (green), in contrast to the freezing point lower bounds (red) of Lin et al. (1) determined by controlled cooling.
The cooling rate we used to get our liquids to crystallize was 600 °C/h, much faster than the 5 °C/h used by Lin et al. (1) in their controlled-cooling crystallizations. Normally, fast cooling rates are expected to increase supercooling (5), and yet we did not observe supercooling during our reversals at 600 °C/h. Nevertheless, we tried a controlled-cooling ramp of 4 °C/h, close to that used by Lin et al. both in air and CO/CO₂ = IW. We consistently find that our first-appearance temperature for crystals is above 1,234 °C. We further lowered the cooling rate to 0.9 °C/h in air; we again produced good crystals by cooling from 1,251 °C to 1,234 °C. Our cooling-rate-independent, minimally supercooled appearance temperatures are not consistent with the results reported by Lin et al. (1) for their controlled cooling in air. Thus, we cannot explain the high fO₂ discrepancy by cooling rate-controlled supercooling. It is possible that there is some other kinetic reason for this difference between our results that arises from configurational differences between our experimental techniques. They use small Pt buckets to contain their charges, whereas we use Pt wire loops with more exposure to the gas stream. Their starting glass was prepared at 1,550 °C, whereas ours was prepared at 1,350 °C. Their near-liquidus phases in air include olivine, whereas ours are just plagioclase and clinopyroxene, reflecting our higher CaO abundance. There are other differences in detail. However, it is also possible that pyrometry artifacts are present and that the differences are not real. If the supercooling reported in air by Lin et al. (1) is confirmed, and is not a pyrometry artifact, it is still not relevant to an equilibrium state because it is not reversible. Kinetic artifacts are of limited interest for the geological time scales of planetary differentiation where the equilibrium states are proven guides.

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