

LETTER



Reply to Walker et al.: Rock melting? Oxygen matters

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Walker et al. (1) were unable to reproduce the lowering of the liquidus temperature of iron-free basalt at high oxygen fugacity (fO_2) reported in our study (2), and claim that, at equilibrium, there is no effect of fO_2 on melting of rocks in the absence of redox-active cations. We repeated the liquidus experiments with a newly calibrated furnace and found an unfortunate pyrometric flaw that can explain the difference between refs. 1 and 2. A correction of ref. 2 has been submitted to PNAS. Reversals of experiments at low fO_2 show that the central tenet of ref. 2, that fO_2 has a significant effect on melt percentages and subliquidus mineralogy, even without redox-active cations, still holds.

Walker et al. (1) suggest that the difference in liquidus temperature between refs. 1 and 2 could be due to reversibility and hysteresis effects, but the reversal experiments from ref. 1 show a fully consistent liquidus with our published nonreversed one at the same low fO_2 (2). We did identify a pyrometric flaw in one subset of our published experiments (2). Control experiments in air performed in two different furnaces at Vrije Universiteit Amsterdam (newly calibrated against the gold melting point), including the furnace used at high fO_2 in ref. 2, yielded crystals + melt at 1,200 °C, consistent with ref. 1 and inconsistent with our previous work (2). The furnace thermocouple was replaced in November 2021 when one of the thermocouple wires broke. We speculate that, before breaking, the thermocouple suffered from degradation, causing a significant pyrometry artifact. The large drop in liquidus temperature at the highest fO_2 in ref. 2 was thus due to incorrect temperature readings. Control experiments found no such pyrometry problems in the other two subseries in ref. 2 performed at lower fO_2 in a different furnace.

We reversed key 1,200 °C experiments at low fO_2 (log $fO_2 = -11$ and -7) reported in ref. 2. Starting materials were first held at 1,000 °C to enable microcrystal growth, and, subsequently, heated rapidly to 1,200 °C, where they were held for 40 h. Run products are characterized by melt containing smaller and more numerous crystals compared to the run product textures in ref. 2, making them more challenging to analyze. Phase assemblages are identical to those reported

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in ref. 2 (orthopyroxene + clinopyroxene + plagioclase + glass). Mass balance calculations yield melt percentages within 2% of the results in ref. 2: 34% at log $fO_2 = -11$, and 59% at log $fO_2 = -7$, confirming that higher fO_2 leads to a higher melt percentage at the same temperature. Orthopyroxene proportions are within 1% of ref. 2. The plagioclase:clinopyroxene ratio is higher, due to the difficulty of obtaining accurate plagioclase analyses given small grain sizes.

In conclusion, a pyrometric flaw in one of the three series of high- fO_2 experiments in ref. 2 is mainly responsible for the difference between ref. 1 and ref. 2. Reversals confirm that fO_2 changes the melting trajectory of rocks without redox-active cations to lower temperatures. Larger effects of fO_2 on melting have been reported in ironbearing compositions at high pressure (3), confirming that fO_2 cannot be ignored when modeling magmatism in rocky (exo)planets.

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